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State of the art on high temperature thermal energy storage for power generation. Part 1—Concepts, materials and modellization

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ABSTRACT

Concentrated solar thermal power generation is becoming a very attractive renewable energy production system among all the different renewable options, as it has have a better potential for dispatchability. This dispatchability is inevitably linked with an efficient and cost-effective thermal storage system. Thus, of all components, thermal storage is a key one. However, it is also one of the less developed. Only a few plants in the world have tested high temperature thermal energy storage systems. In this paper, the different storage concepts are reviewed and classified. All materials considered in literature or plants are listed. And finally, modellization of such systems is reviewed.

Contents

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1. Introduction

Nowadays, carbon dioxide is responsible for more than 50% of the man-made greenhouse effect, making it the most important contributor to climate change. It is produced mainly by the burning of fossil fuels. Because of the time lapse between emissions and their effects, the full consequences of developing climate change have still to emerge over the coming decades, bringing increased danger to the stability of the world's economy and lifestyle.

Solar thermal power involves hardly any of the polluting emissions or environmental safety concerns associated with conventional, fossil or nuclear-based power generation. There is very little pollution in the form of exhaust gases, dust or fumes. Most importantly, in terms of the global environment, there are no emissions of carbon dioxide in solar-only operation of a solar thermal plant—the main gas responsible for global climate change.

Solar thermal power plants produce electricity in the same way as other conventional power plants, but using solar radiation as energy input. This energy can be transformed to high-temperature steam, to drive a turbine or a motor engine.

Mainly, four elements are required in these plants: concentrator, receiver, transport/storage media system, and power conversion device. Of all components, thermal storage is a key component. However, it is also one of the less developed. Only a few plants in the world have tested high temperature thermal energy storage systems. In this context, high temperature is considered when storage is performed between 120 and 600 °C.

Here, a review of the storage media systems is presented, focussed on the storage concepts and classification, materials and material properties, and modellization. In a second paper some case studies are presented [1].

2. Energy storage

2.1. Definition

Energy storage (ES) is the storing of some form of energy that can be drawn upon at a later time to perform some useful operation.

A device that stores energy is sometimes called an accumulator. All forms of energy are either potential energy (e.g. chemical or gravitational), kinetic energy, electrical energy or thermal energy, and all these forms of energy could be stored with an appropriate method, system or technology. That means that every form of energy has itself an accumulator.

As Fig. 1 shows, a large variety of energy storage systems are under development [2]. Thermal energy storage (TES) will be discussed in this document, because it is the best method to be applied in solar power plants.

2.2. Thermal energy storage

2.2.1. Definition

Thermal energy storage (TES) systems have the potential of increasing the effective use of thermal energy equipment and of facilitating large-scale switching. They are normally useful for correcting the mismatch between the supply and demand of energy.

There are mainly two types of TES systems, sensible storage systems and latent storage systems. As the temperature of a substance increases, its energy content also increases. The energy released (or absorbed) by a material as its temperature is reduced (or increased) is called sensible heat.

On the other hand, the energy required to convert a solid material in a liquid material, or a liquid material in a gas (phase change of a material) is called heat of fusion at the melting point (solid to liquid) and heat of vaporization (liquid to gas), respectively. Latent heat is associated with these changes of phase.

The other category of storing heat is through the use of reversible endothermic chemical reactions. Chemical heat is associated to these reversible chemical reactions where heat is needed to dissociate a chemical product. All this heat (or almost all) will be recuperated later, when synthesis reaction takes place.

A complete storage process involves at least three steps: charging, storing and discharging. In practical systems, some of the steps may occur simultaneously, and each step can happen more than once in each storage cycle [3].

In terms of storage media, a wide variety of choices exists depending on the temperature range and application.

2.2.2. Design criteria

Several facts have to be considered when deciding on the type and the design of any thermal storage system. A key issue in the design of a thermal energy storage system is its thermal capacity. However, selection of the appropriate system depends on many cost-benefit considerations, technical criteria and environmental criteria.

The cost of a TES system mainly depends on the following items: the storage material itself, the heat exchanger for charging and discharging the system and the cost of the space and/or enclosure for the TES.

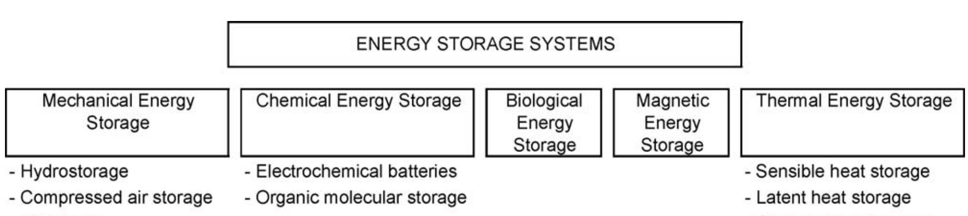


Fig. 1. Classification of energy storage systems [2].

From the technical point of view, the most important requirements are: high energy density in the storage material (storage capacity); good heat transfer between heat transfer fluid (HTF) and storage medium (efficiency); mechanical and chemical stability of storage material (must support several charging/discharging cycles); compatibility between HTF, heat exchanger and/or storage medium (safety); complete reversibility of a number of charging/discharging cycles (lifetime); low thermal losses; and ease of control.

And finally, the most important design criteria from the point of view of technology are: operation strategy; maximum load; nominal temperature and specific enthalpy drop in load; and integration into the power plant. All these criteria have to be considered when deciding on the type and design of thermal storage.

2.2.3. Storage media

2.2.3.1. Sensible heat storage. Thermal energy can be stored in the change of temperatures of substances that experience a change in internal energy. Besides the density and the specific heat of the storage material, other properties are important for sensible heat storage: operational temperatures, thermal conductivity and diffusivity, vapour pressure, compatibility among materials stability, heat loss coefficient as a function of the surface areas to volume ratio, and cost.

Sensible TES consists of a storage medium, a container (commonly tank) and inlet/outlet devices. Tanks must both retain the storage material and prevent losses of thermal energy. The existence of a thermal gradient across storage is desirable.

Sensible heat storage can be made by solid media or liquid media. Solid media (for the temperature range studied in this paper, mainly high temperature concrete and castable ceramics) are usually used in packed beds, requiring a fluid to exchange heat. When the fluid is a liquid, heat capacity of the solid in the packed bed is not negligible, and the system is called dual storage system. Packed beds favour thermal stratification, which has advantages.

An advantage of a dual system is the use of inexpensive solids such as rock, sand or concrete for storage materials. Concrete, for example, is chosen because of its low cost, availability throughout and easy processing. Moreover, concrete is a material with high specific heat, good mechanical properties (e.g. compressive strength), thermal expansion coefficient near that of steel (pipe material) and high mechanical resistance to cyclic thermal loading. When concrete is heated, a number of reactions and transformations take place which influence its strength and other physical properties: compressive strength decreases about a 20% at 400 °C, the specific heat decreases in the range of temperature between 20 and 120 °C, and the thermal conductivity decreases between 20 and 280 °C. Resistance to thermal cycling depends on the thermal expansion coefficients of the materials used in the concrete. To minimize such problems, a basalt concrete is sometimes used. Steel needles and reinforcement are sometimes added to the concrete to impede cracking. At the same time, by doing so, the thermal conductivity is increased about 15% at 100 °C and 10% at 250 °C. On the other hand, rock is an inexpensive TES material from the standpoint of cost.

Liquid media (mainly molten salts, mineral oils and synthetic oils) maintain natural thermal stratification because of density differences between hot and cold fluid. The existence of a thermal gradient across storage is desirable. The requirements to use this characteristic are that the hot fluid is supplied to the upper part of storage during charging, and the cold fluid is extracted from the bottom part during discharging, or using another mechanism to ensure that the fluid enters the storage at the appropriate level in accordance with its temperature, in order to avoid mixing. This can be done by some stratification devices (floating entry, mantle heat exchange, etc.).

Different materials can be used as liquid media silicon and synthetic oils (very expensive materials), and nitrites in salts (with potential corrosion problems).

2.2.3.2. Latent heat storage media. Thermal energy can be stored nearly isothermally in some substances as the latent heat of phase change, as heat of fusion (solid–liquid transition) or heat of vaporization (liquid–vapour transition). Nowadays, mainly the solid–liquid transition is used, and substances used under this technology are called phase change materials (PCM).

Storage systems utilizing PCM can be reduced in size compared to single-phase sensible heating systems. However, heat transfer design and media selection are more difficult, and experience with low temperature salts has shown that the performance of the materials can degrade after moderate number of freeze–melt cycles.

Phase change materials allow large amounts of energy to be stored in relatively small volumes, resulting in some of the lowest storage media costs of any storage concepts.

2.2.3.3. Chemical heat storage. A third storage mechanism is by means of chemical reactions. For this type of storage it is necessary that the chemical reactions involved are completely reversible. The heat produced by the solar receiver is used to excite an endothermic chemical reaction. If this reaction is completely reversible the thermal energy can be recovered completely by the reverse reaction.

Common advantages of this mechanism are high storage energy densities, indefinitely long storage duration at near ambient temperature and heat-pumping capability. Nonetheless, the development level of reversible thermochemical reaction (RTR) is already at a very early stage.

This kind of storage media is a truly attractive option in longer term and could offer relatively low costs [4]. Solar thermal technologies via thermochemical conversion paths offer the prospect of systems with inherent energy storage for continuous (24 h) generation of electricity. This issue will be increasingly significant as the world moves towards a truly renewable energy based economy.

2.2.4. Storage concept

2.2.4.1. Classification. High temperature storage concepts in solar power plants can be classified as active or passive systems (Fig. 2).

An active storage system is mainly characterized by forced convection heat transfer into the storage material. The storage medium itself circulates through a heat exchanger (this heat exchanger can also be a solar receiver or a steam generator). This system uses one or two tanks as storage media.

Active systems are subdivided into direct and indirect systems. In a direct system, the heat transfer fluid serves also as the storage medium, while in an indirect system, a second medium is used for storing the heat.

Passive storage systems are generally dual medium storage systems: the HTF passes through the storage only for charging and discharging a solid material. The HTF carries energy received from

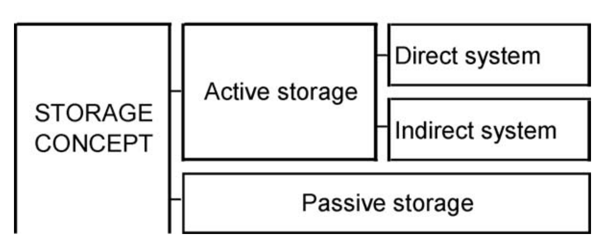


Fig. 2. Scheme of classification of different storage systems according the storage concept.

the energy source to the storage medium during charging, and receives energy from the storage when discharging (these systems are also called regenerators).

The main disadvantage of regenerators is that the HTF temperature decreases during discharging as the storage material cools down. And one more problem is that the heat transfer is rather low, and usually there is no direct contact between the HTF and the storage material as the heat is transferred via a heat exchanger.

2.2.4.2. Active storage systems. Active direct storage systems: in an active direct system, in the up to now developed solar systems the HTF used in the solar field is also used as storage material. That means the material must reach particularly characteristics to be a good HTF and a good storage material, at the same time.

The use of molten salts or steam as a HTF and storage material at the same time eliminates the need for expensive heat exchangers. It allows the solar field to be operated at higher temperatures than current heat transfer fluids allow. This combination also allows for a substantial reduction in the cots of TES system, improving the performance of the plant and reducing the levelized electrical cost (LEC). But in the case of the molten salts, they freeze at relatively high temperatures (120–220 °C), and this means that special care must be taken to ensure that the salt do not freeze in the solar field piping during the night. Hence, routine freeze protection operation must be done by the thermal storage, increasing maintenance and operation (M&O) costs. On the other hand, results reported by D. Kearney concluded that the use of the molten salt as a HTF made economic sense only if the solar plant included a thermal storage system [5,6].

Since the freezing point of currently used molten salts is considerably high, special attention has to be dedicated to freeze protection operation: the HTF is circulated through the solar field during the whole night, in order to maintain piping warm and avoid critical thermal gradients during start-up; if the HTF temperature falls below a certain value, an auxiliary heater is used to maintain the minimum value.

One of the active direct systems is the two tanks direct system, which consists in a storage system where the HTF is directly stored in a hot tank, in order to use it during cloudy periods or nights. The cooled HTF is pumped to the other tank, cold tank, where it remains waiting to be heated one more time [7]. Fig. 3 shows the scheme of the plant Solar Tres, that uses molten salts ($NaNO_3$ and KNO_3) as HTF. Solar Tres is placed on Fuentes de Andalucia, near to Seville (Spain) and was built during 2008.

The advantages of the two tanks solar systems are: cold and heat storage materials are stored separately; low-risk approach; possibility to raise the solar field output temperature to 450/500 °C (in trough plants), thereby increasing the Rankine cycle efficiency of the power block steam turbine to the 40% range (conventional plants have a lower efficiency) [6]; and the HTF temperature rise in the collector field can increase up to a factor of 2.5 compared to Solar Two experience (located in Daggett, CA, built in 1995 and decommissioned in 1999), reducing the physical size of the thermal storage system [6,7].

The disadvantages are very high cost of the material used as a HTF and storage material; high cost of the heat exchangers, the need of using two tanks instead of one; relatively small temperature difference between the hot and the cold fluid in the storage system; very high-risk of solidification of storage fluid, due to its relatively high freeze point (which increases the M&O costs); the high temperature of both tanks drives to an increase of losses in the solar field; and the lowest cost TES design and operation does not correspond to the lowest cost of electricity (usually at night) [9].

Active indirect storage systems: within the indirect systems, one can find the two tanks indirect system and the single tank system (also called thermocline system). The two tanks system is called indirect system because the heat transfer fluid which is circulating in the solar field is different from the one for the storage medium (thermal energy storage media). It has been developed in recent years.

The two tanks indirect system consists, like the direct system, in two tanks where the energy is stored not directly by the HTF, but by a second heat fluid (generally oil), heated thanks to the HTF pumped through heat exchanger. Heat from the HTF is absorbed in the oil-to-salt heat exchanger by a thermal energy storage (TES) media, normally molten salts (Fig. 4).

As in the other two tanks case, one of the tanks serves to store hot storage material, and the other one, to receive the cold storage

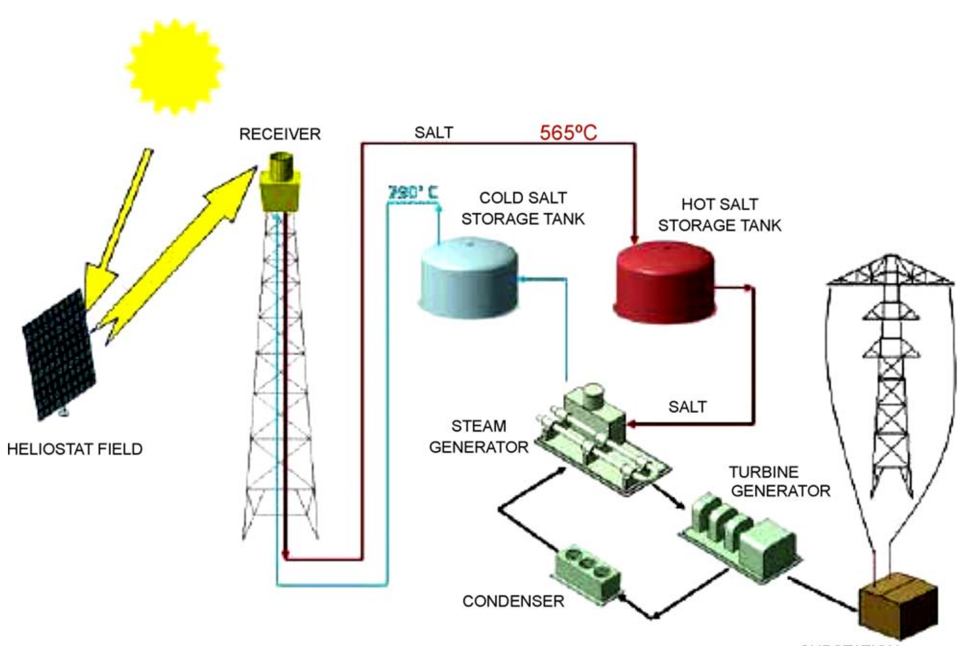


Fig. 3. Scheme of installation of a central tower power plant (Planta Solar Tres), with direct two-tanks and mineral oil like storage system [8].

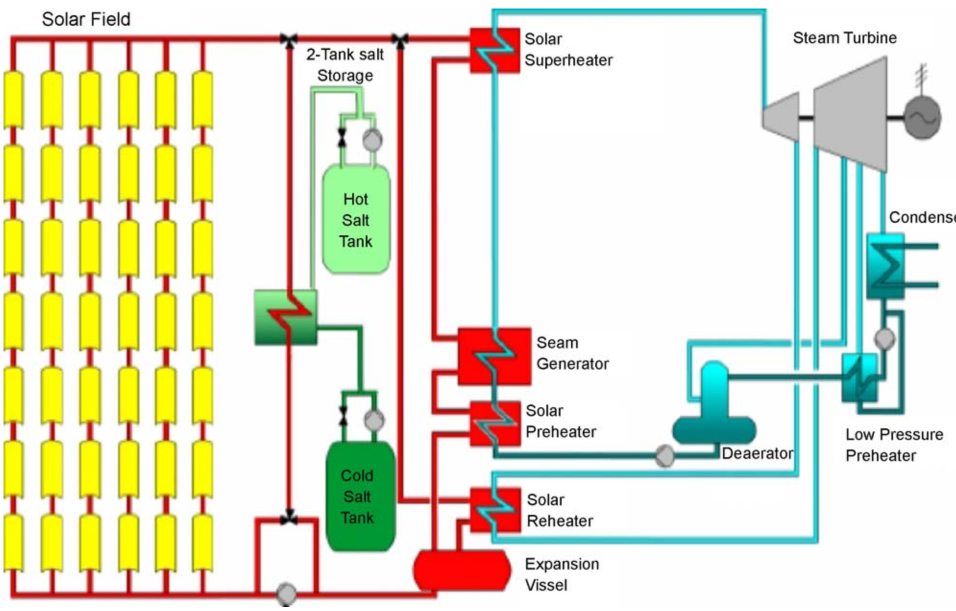


Fig. 4. Scheme of installation of a parabolic through power plant, with two-tanks storage system [10].

material. During a thermal storage charge cycle, a portion of the oil from the collector field is directed to the oil-to-salt heat exchanger, where the oil cools from the nominal inlet temperature of 391 °C to an outlet temperature of about 298 °C. Nitrate salt from the cold storage tank flows in a counter current arrangement through the heat exchanger. The salt is heated from an inlet temperature of 291 °C to an outlet temperature of 384 °C, and then stored in the hot storage tank. During the discharge cycle, the oil and salt flow paths are reversed in the oil-to-salt heat exchanger. Heat is then transferred from the salt to the oil to provide the thermal energy for the steam generator.

The advantages of the two tanks indirect system are (similarly to the direct systems): cold and hot HTF are stored separately; and the storage material flows only between hot and cold tanks, not through the parabolic troughs. The disadvantages are the same as in the two tanks direct systems.

Another active indirect storage system is the single tank system, where hot and cold fluids are stored in the same tank. This system provides one possibility for further reducing the cost of a direct two-tank storage system. Here the hot and cold fluids are separated because of the stratification, and the zone between the hot and cold fluids is called the thermocline. The thermocline storage system features the hot fluid on top and the cold fluid on the bottom. In these systems, the HTF which arrives from the solar field passes through a heat exchanger, heating the thermal storage fluid media. This fluid is stored in a single tank. Usually a filler material is used to help the thermocline effect. Experimental studies performed up to now found that this filler material acts as the primary thermal storage medium, but selection of other storage and filler material can change this.

Sandia National Laboratories identified quartzite rock and silica sands as potential filler materials [11]. Results demonstrated that both materials appear able to withstand the molten salt environment quite well (no significant deterioration).

Depending on the cost of the storage fluid, the thermocline can result in a substantially low cost storage system. This system has

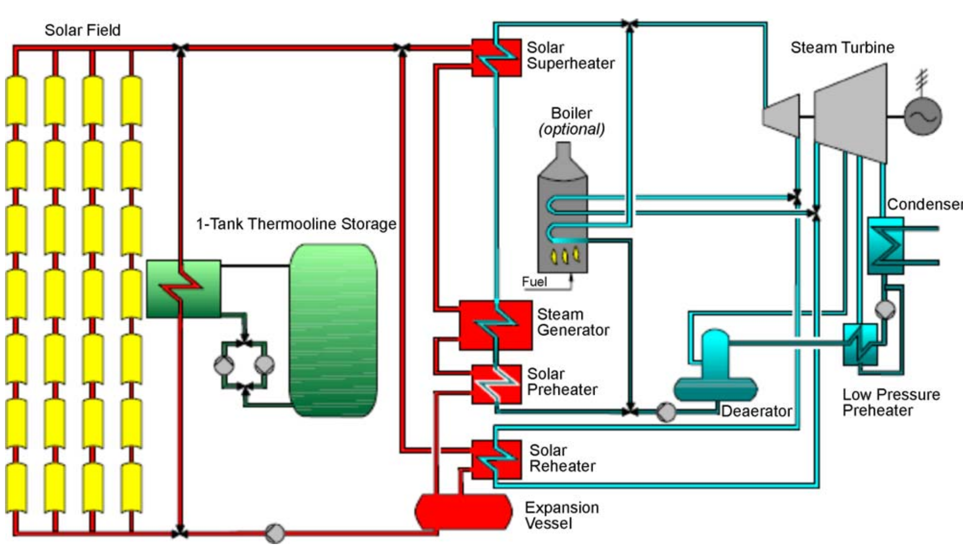


Fig. 5. Scheme of installation of a parabolic through power plant, with single-tank storage system [10].

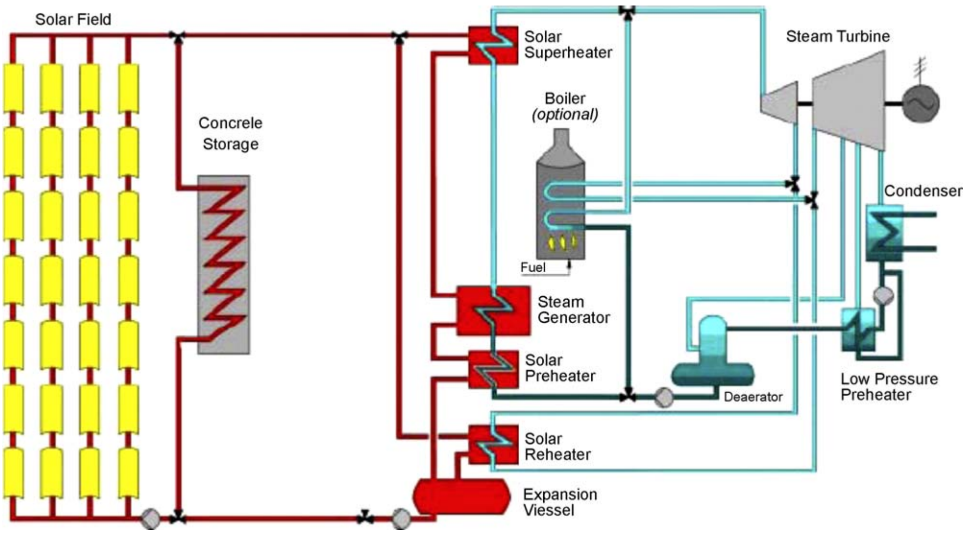


Fig. 6. Scheme of a parabolic through power plant, with concrete (or castable ceramics) storage system [10].

an additional advantage: most of the storage fluid can be replaced with a low cost filler material, for example, quartzite rock and sand (Fig. 5).

The advantages of the single tank thermocline system are: decrease of storage tanks cost, because of this system uses only one tank; low cost of the filler materials (rocks and sand); therefore, according to Brosseau et al. [11], thermocline system is about 35% cheaper than the two tank storage system.

The disadvantages are relatively high freezing points of most molten salts formulations (it is necessary to maintain a minimum system temperature to avoid freezing and salt dissociation); it is more difficult to separate the hot and cold HTF; the high outlet temperature drives to an increase of losses in the solar field; maintaining the thermal stratification requires a controlled charging and discharging procedure, and appropriate methods or devices to avoid mixing; design of storage system is complex; and thermodynamically, it is an inefficient power plant [12].

2.2.4.3. Passive storage systems. In a passive storage system the heat transfer medium passes through the storage only for charging or discharging the system. The storage medium itself does not circulate. Passive systems are generally dual medium storage systems (these systems are also called regenerators). Passive storage systems are mainly solid storage systems (concrete and castable materials, and PCM).

In the concrete storage case, the solar energy of the solar field is transferred from the HTF to the solid storage material system. The storage material contains a tube heat exchanger to transfer the thermal energy from the HTF to the storage (Fig. 6). A tubular heat exchanger is integrated into the storage material. This heat exchanger demands a significant share of the investment costs. The design of the geometry parameters like tube diameter and number of pipes is also important for the final result.

These solid media sensible heat storage units were developed in the project "Midterm Storage Concepts—Further Development of Solid Media Storage Systems" founded by the German government from December 2001 to December 2003 [13]. The focuses of this project were the development of an efficient and cheap sensible storage material, and the demonstration of this technology with a 350 kW/h test unit.

The advantages of concrete systems are very low cost of thermal energy storage media; high heat transfer rates into and out of the solid medium (due to a good contact between the concrete and piping); facility to handling of the material; and low degradation of heat transfer between the heat exchanger and the storage material. The disadvantages are increase of cost of heat exchanger and of engineering; and long-term instability.

Another passive system is the use of phase change materials as storing material. The overall concept of the storage system is the same as in solid systems, but the storing material is a material with a melting temperature within the range of the charging and discharging temperatures of the HTF. This concept has been developed with the European project DISTOR [14]. Within this project the definition of storage design specifications, operation conditions, and control options of a TES system for DSG CSP plants were set. The binary PCM $NaNO_3/KNO_3$ was defined as basic storage material and measures for improving thermal conductivity were successfully developed (Fig. 7). Graphite fin tube—"sandwich" design concept proved to be feasible for scale up.

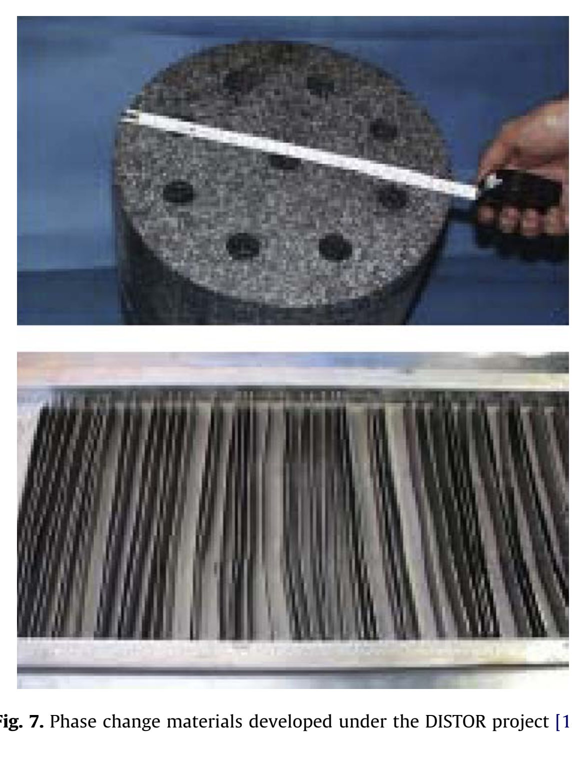


Fig. 7. Phase change materials developed under the DISTOR project [14].

Table 1
Main characteristics of sensible heat storage solid materials [4,10].

Storage medium	Temperature		Average density (kg/m^3)	Average heat conductivity (W/m K)	Average heat capacity (kJ/kg K)	Volume specific heat capacity (kWh$_t$/m^3)	Media costs per kg (US$/kWh$_t$)	Media costs per kWh$_t$ (US$/kWh$_t$)
	Cold (°C)	Hot (°C)						
Sand-rock-mineral oil	200	300	1700	1.0	1.30	60	0.15	4.2
Reinforced concrete	200	400	2200	1.5	0.85	100	0.05	1.0
NaCl (solid)	200	500	2160	7.0	0.85	150	0.15	1.5
Cast iron	200	400	7200	37.0	0.56	160	1.00	32.0
Cast steel	200	700	7800	40.0	0.60	450	5.00	60.0
Silica fire bricks	200	700	1820	1.5	1.00	150	1.00	7.0
Magnesia fire bricks	200	1200	3000	5.0	1.15	600	2.00	6.0

In 1993, DLR–ZSW proposed a hybrid PCM-sensible-PCM storage as storage system for a solar plant. This kind of system combines characteristics of latent and sensible heat storage systems.

The advantages of these storage systems are better use of PCM storage capacities; reduction of costs, comparing with storage systems with only PCM as storage media; and improve of storage ratio, comparing with systems with only sensible heat materials. The disadvantages are that it is necessary to develop technologies to transfer this concept.

3. High temperature thermal energy storage materials

3.1. Materials

3.1.1. Sensible heat storage materials

Sensible heat storage materials are defined as a group of materials which undergo no change in phase over the temperature range encountered in the storage process. The amount of thermal energy stored in a mass of material can be expressed as:

$$Q = \rho \cdot \bar{c}_p \cdot V \cdot \Delta T \quad (1)$$

where Q is the amount of heat stored [J], ρ is the density of the storage material [kg/L], $\bar{c}_p$ is the specific heat over the temperature range of operation [J/(kg K)], V is the volume of storage material used (L), and ΔT is the temperature range of operation [°C].

The ability to store sensible thermal energy for a given material depends strongly on the value of the quantity $\rho \cdot \bar{c}_p$, the thermal capacity. For a material to be useful in a TES application, it must be inexpensive and have good thermal capacity. Another important parameter in sensible TES is the rate at which that heat can be released and extracted. This characteristic is function of the thermal diffusivity.

It is possible to store thermal energy by sensible heat in solid or liquid materials.

Concerning solid materials, concrete and castable ceramics are the more studied, most of all due to their low price and good thermal conductivities. Concrete or castable ceramics (both tested at the Plataforma Solar de Almeria) present good characteristics to be used as a solid heat storage materials [15,16]. Table 1 shows the main characteristics of the most common solid thermal storage materials found in the literature [4,10].

In recent years, studies by the DLR in Stuttgart have shown that concrete is a good solution to be applied in thermal storage, due mainly to its low cost, facility of handling and structural stability. In order to improve the soft characteristics of concrete, a new high temperature concrete was studied, resulting the characteristic values shown in Table 2 [17].

A comparison between characteristics of high temperature concrete and castable ceramics is shown in Table 3.

On the other side, concerning liquid materials, a variety of fluids have been tested to transport the heat, including water, air, oil, and sodium, before molten salts were selected as best. Molten salts are used in solar power tower systems because they are liquid at atmospheric pressure, provide an efficient, low cost medium in which to store thermal energy, their operating temperatures are compatible with today's high-pressure and high-temperature steam turbines, and they are non-flammable and non-toxic. In addition, molten salts are used in the chemical and metals industries as heat-transport fluid, so experience with molten-salt systems exists for non-solar applications [19,20].

The two leading candidates are the so-called solar salt and a salt sold commercially as HitecXL. The so-called solar salt is a binary salt consisting of 60% $NaNO_3$ and 40% KNO_3, the salt melts at 221 °C and is kept liquid at 288 °C in an insulated cold storage tank. The salt sold commercially as HitecXL is a ternary salt consisting of 48% $Ca(NO_3)_2$, 7% $NaNO_3$, and 45% KNO_3 [21], whose behaviour was analysed in PSA and Themis plants. This salt was developed as a second tentative from Hitec (a eutectic mixture of 40% $NaNO_2$, 7% $NaNO_3$ and 53% KNO_3, with 142 °C melt–freeze point) [4,21].

An Italian research laboratory, ENEA, has proven the technical feasibility of using molten salts in a parabolic trough solar field with salt mixtures that freeze at 220 °C. And Sandia National Laboratories are developing new salt mixtures with the potential for freezing points below 100 °C (beyond 100 °C the freezing problem is expected to be more manageable).

Experiences led by Kearny and Associates [5,11], evaluated the option of using molten salts as HTF, and concluded the existence of important disadvantages, like the relative high freezing point of most molten salts, and the fact that their higher outlet temperature means heat losses from the solar heat, requiring more expensive piping and materials.

Table 2
Properties of high temperature concrete storage material [17].

Material	High temperature concrete
Density at 200 °C [kg/m^3]	2700
Specific heat capacity at 200 °C [J/kg K]	910
Thermal conductivity at 200 °C [W/m K]	1.0
Coefficient thermal expansion at 200 °C [10^{-6}/K]	9.3
Capacity [kWh/m^3 K]	0.68

Table 3
Material properties of storage materials developed at DLR (Stuttgart, Germany) [18].

Material	Castable ceramic	High temperature concrete
Density [kg/m^3]	3500	2750
Specific heat at 350 °C [J/kg K]	866	916
Thermal conductivity at 350 °C [W/m K]	1.35	1.0
Coefficient of thermal expansion at 350 °C [10^{-6}/K]	11.8	9.3

Table 4
Main characteristics of sensible heat storage liquid materials [10,12].

Storage medium	Temperature		Average density (kg/m^3)	Average thermal conductivity (W/m K)	Average heat capacity (kJ/kg K)	Volume specific heat capacity (kWh_t/m^3)	Media costs per kg ($US\$/kWh_t$)	Media costs per kWh_t ($US\$/kWh_t$)
	Cold (°C)	Hot (°C)						
HITEC solar salt	120	133	–	–	–	–	–	–
Mineral oil	200	300	770	0.12	2.6	55	0.30	4.2
Synthetic oil	250	350	900	0.11	2.3	57	3.00	43.0
Silicone oil	300	400	900	0.10	2.1	52	5.00	80.0
Nitrite salts	250	450	1825	0.57	1.5	152	1.00	12.0
Nitrate salts	265	565	1870	0.52	1.6	250	0.50	3.7
Carbonate salts	450	850	2100	2.0	1.8	430	2.40	11.0
Liquid sodium	270	530	850	71.0	1.3	80	2.00	21.0

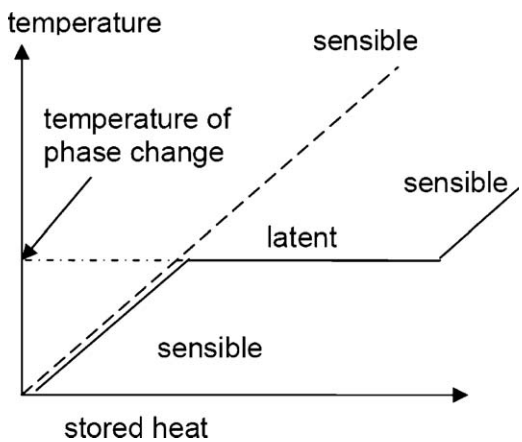


Fig. 8. Phase change profile of PCM [24].

Table 4 presents the characteristics of different materials used in sensible heat storage. Within the materials presented, the HITEC Solar Salt, a commercial nitrate salt developed and used in the Themis solar plant and in PSA is included. Its composition of this ternary salt is 44% $CaNO_3$, 12% $NaNO_3$, and 44% KNO_3, and the lowest freezing range is about 120 and 133 °C.

The main desired characteristics of a molten salt, to be used in this technology are high density, low vapour pressure, moderate specific heat, low chemical reactivity, and low cost. Only a limited number of molten salts accomplish these requirements. In fact, one of the disadvantages of molten salts is their cost [22,23].

3.1.2. Latent heat storage materials

Storage systems based on phase change materials with solid–liquid transition are considered to be an efficient alternative to sensible thermal storage systems. From an energy efficiency point of view, PCM storage systems have the advantage that they operate with small temperature differences between charging and discharging (Fig. 8). Furthermore, these storages have high energy densities compared to sensible heat storages.

The most interesting phase change to be applied in a thermal storage is the phase change solid–liquid. Fig. 9 shows a scheme with the families of materials which could be used as phase change materials in thermal energy storage systems.

The development of effective thermal energy storage systems using PCM is increasing the interest, due to the potential improvement in energy efficiency, storing and releasing thermal energy at nearly constant temperature [26]. But most PCM have low thermal conductivity, and that leads to slow charging and discharging rates [27].

Nowadays there are several PCM commercial materials (Table 5). At the same time, there are also several materials, classified as organic or inorganic materials, with potential to be used as PCM (Tables 6 and 7). These tables include the main characteristics of each of these materials.

PCM present different problems that must be overcome to be successfully used in any application. Low thermal conductivity of

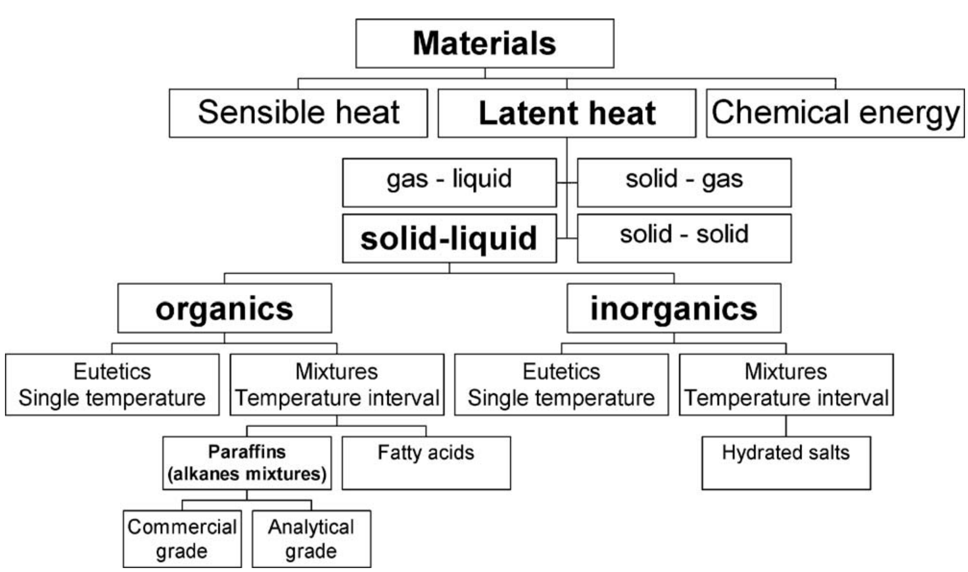


Fig. 9. Classification of latent heat materials, with phase change solid–liquid [25].

Table 5
Commercial PCM materials from EPS (United Kingdom) and Rubitherm (Germany) [28,29].

Name	Type	Manufacturer	Phase change temperature (°C)	Density (kg/m^3)	Latent heat (kJ/kg)	Latent heat (MJ/m^3)	Specific heat (kJ/kg K)	Thermal conductivity (W/m K)
RT110	Paraffin	Rubitherm	112	n.a.	213	n.a.	n.a.	n.a.
E117	Inorganic	EPS	117	1450	169	245	2.61	0.70
A164	Organic	EPS	164	1500	306	459	n.a.	n.a.

n.a.: Not available.

Table 6
Inorganic substances with potential use as PCM [25].

Compound	Melting temperature (°C)	Heat of fusion (kJ/kg)	Density (kg/m^3)	Specific heat (kJ/kg K)	Thermal conductivity (W/m K)
$MgCl_2\cdot 6H_2O$	117 [30–33] 115 [34] 116 [25]	168.6 [30,33] 165 [31,25]	1450 (liquid, 120 °C) [30,33] 1442 (liquid, 78 °C) [35] 1569 (solid, 20 °C) [30,33] 1570 (solid, 20 °C) [25]	n.a.	0.570 (liquid, 120 °C) [30,33] 0.598 (liquid, 140 °C) [33] 0.694 (solid, 90 °C) [30,33] 0.704 (solid, 110 °C) [33]
Hitec: KNO_3–$NaNO_2$–$NaNO_3$	120 [7]	n.a.	n.a.	n.a.	n.a.
Hitec XL: 48%$Ca(NO_3)_2$–45%KNO_3–7%$NaNO_3$	130 [7]	n.a.	n.a.	n.a.	n.a.
$Mg(NO_3)\cdot 2H_2O$	130 [34]	n.a.	n.a.	n.a.	n.a.
KNO_3–$NaNO_2$–$NaNO_3$	132 [36]	275 [36]	n.a.	n.a.	n.a.
68% KNO_3–32%$LiNO_3$	133 [37]	n.a.	n.a.	n.a.	n.a.
KNO_3–$NaNO_2$–$NaNO_3$	141 [36]	75 [36]	n.a.	n.a.	n.a.
Isomalt	147 [36]	275 [36]	n.a.	n.a.	n.a.
$LiNO_3$–$NaNO_3$	195 [36]	252 [36]	n.a.	n.a.	n.a.
40%KNO_3–60%$NaNO_3$	220 [7]	n.a.	n.a.	n.a.	n.a.
54% KNO_3–46%$NaNO_3$	220 [37]	n.a.	n.a.	n.a.	n.a.
$NaNO_3$	307 [35] 308 [4,38]	172 [35] 174 [38] 199 [4]	2260 [35] 2257 [4]	n.a.	0.5 [4]
KNO_3/KCl	320 [39]	74 [39]	2100 [39]	1.21 [39]	0.5 [39]
KNO_3	333 [4] 336 [38]	266 [3] 116 [38]	2.110 [38]	n.a.	0.5 [38]
KOH	380 [4]	149.7 [4]	2.044 [4]	n.a.	0.5 [4]
$MgCl_2$/KCl/NaCl	380 [39]	400 [39]	1800 [39]	0.96 [39]	n.a.
$AlSi_{12}$	576 [40]	560 [40]	2700 [40]	1.038 [40]	160 [40]
$AlSi_{20}$	585 [40]	460 [40]	n.a.	n.a.	n.a.
$MgCl_2$	714 [35]	452 [35]	2140 [35]	n.a.	n.a.
80.5% LiF–19.5% CaF_2 eutetic	767 [41]	790 [41]	2100/2670[a] [41]	1.97/1.84[a] [41]	1.7/5.9[a] [41]
NaCl	800 [35] 802 [4]	492 [35] 466.7 [4]	2160 [4,35]	n.a.	5 [4]
$NaCO_3$–$BaCO_3$/MgO	500–850 [10]	n.a.	2600 [10]	n.a.	5 [10]
LiF	850 [42]	1800 MJ/m^3 [42]	n.a.	n.a.	n.a.
Na_2CO_3	854 [4,10]	275.7 [4]	2533 [4,10]	n.a.	2 [4,10]
KF	857 [35]	452 [35]	2370 [35]	n.a.	n.a.
K_2CO_3	897 [4,10]	235.8 [4]	2290 [4,10]	n.a.	2 [4,10]
KNO_3/$NaNO_3$ eutetic	n.a.	94.25 [4,43]	n.a.	n.a.	0.8 [4,43]

n.a.: Not available.
[a] Liquid phase.

Table 7
Organic materials with potential use as PCM [25].

Compound	Melting temperature (°C)	Heat of fusion (kJ/kg)	Heat of fusion (kJ/L)
Isomalt $((C_{12}H_{24}O_{11}\cdot 2H_2O)+(C_{12}H_{24}O_{11}))$	147 [36]	275 [36]	n.a.
Adipic acid	152 [36]	247 [36]	n.a.
Dimethylol propionic acid	153 [36]	275 [36]	n.a.
Pentaerythritol	187 [36]	255 [36]	n.a.
AMPL $((NH_2)(CH_3)C(CH_2OH)_2)$	112 [44]	28.5 [44]	2991.4 [44]
TRIS $((NH_2)\ C(CH_2OH)_3)$	172 [44]	27.6 [44]	3340 kJ/kmol [44]
NPG $((CH_3)_2C(CH_2OH)_2)$	126 [44]	44.3 [44]	4602.4 kJ/kmol [44]
PE $(C(CH_2OH)_4)$	260 [44]	36.9 [44]	5020 kJ/kmol [44]

n.a.: Not available.

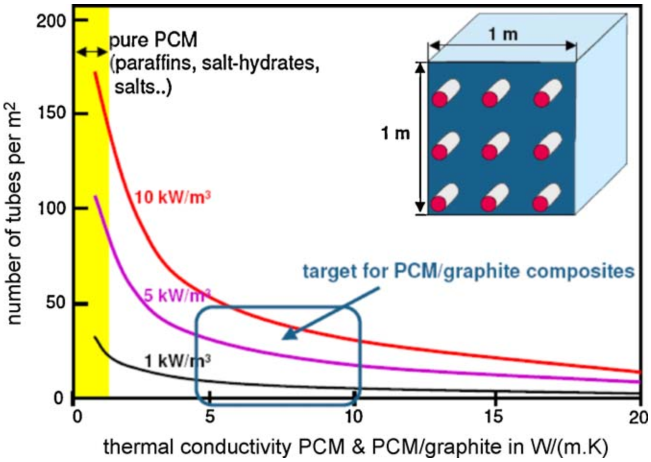


Fig. 10. Thermal conductivity of pure PCM, and target for PCM/graphite composites [46].

available PCM is one of the problems, solid deposits on the heat transfer surfaces is another.

In order to improve the low thermal conductivity of pure PCM, two approaches are possible: the improvement of heat transfer using mass transfer, which is convection (convection only occurs in the liquid phase), and the improvement of heat transfer through increasing the thermal conductivity (this can be achieved adding objects with larger thermal conductivity to the pure PCM) [45].

To improve thermal conductivity in PCM storage systems, one possibility is the use of composite latent heat storage materials (CLHSM). Here, the good thermal conductivity of an additive material and the properties of a high latent heat of the PCM are combined. One of the most common materials added to PCM is the graphite. The PCM/graphite composites have a thermal conductivity between 5 and 10 W/m K, while PCM have thermal conductivities around 0.2–0.8 W/m K (Fig. 10). This value depends on the quantity of graphite imbedded on the PCM [47,48].

3.1.3. Chemical heat storage materials

The technology of thermal energy storage utilizing the heat of chemical reactions has the possibility to realize higher energy efficient processes than other thermal energy storage technologies [49]. The main advantage of using chemical reactions as storage systems is the potentially high energy density.

Table 8 presents several reactions that have been investigated to be used as chemical storage materials. In this state of the art only the most relevant chemical processes for thermal storage will be described: reactions metal oxide/metal (SnO_x/Sn) and ammonia.

In reactions metal oxide/metal (SnO_x/Sn), according to Foster [21], the reaction is possible and technical feasible, considering reactions below:

$$SnO_2 + 2CH_4 + heat \rightarrow Sn + 2CO + 4H_2 \quad (R1)$$

$$Sn + 2H_2O \rightarrow SnO_2 + 2H_2 + heat \quad (R2)$$

Concentrated solar energy will be increasing the temperature in reactor (Fig. 11). Reaction (R1) takes place at 980 K and SnO_2 is reduced with CH_4. At these temperatures, SnO_2 is solid (dust), and floats on the top of liquid Sn in a solar reactor. This simplifies considerably the concept and construction of the solar reactor.

An addition of CH_4 produces the SnO_x dissociation, and the Sn liquid at 980 K approximately is stored in a tank. In cloudy periods or nights, Sn passes through the heat exchanger. Cold Sn is sent to a tank where H_2O vapour is added, taking place reaction (R2). In this way, SnO_2 can be recuperated to restart the process.

The critical point of this device is the kinetic behaviour of reactions [21]. Although the reaction is feasible with solar energy, technically, this way is not still developed, and it is necessary to increase the investigation.

Ammonia is a pungent smelling gas which is used in the production of fertilizers and cleaning agents among other applications. Production of ammonia is one of the world's largest chemical process industries, with in excess of 125 million tonnes produced annually. In a modern ammonia plant, the exothermic reaction heat from ammonia synthesis converters is routinely converted to superheated steam suitable for electric power generation in conventional Rankine cycle systems [15].

In this system, liquid ammonia (NH_3) is dissociated in an energy storing (endothermic) chemical reactor as it absorbs solar thermal energy [28,58–61]. At a later time and place, the reaction products, hydrogen (H_2) and nitrogen (N_2), react in an energy-releasing (exothermic) reactor to re-synthesis ammonia (Fig. 12) [62].

$$2NH_3 + heat \rightarrow N_2 + 3H_2 \quad (R3)$$

$$N_2 + 3H_2 \rightarrow 2NH_3 + heat \quad (R4)$$

3.2. Material properties

Thermal energy storage materials must accomplish basic characteristics to be used (Table 9) [25]. Based on these characteristics, the appropriate material for a determinate application can be found.

3.3. Material properties analysis

The main thermal properties to study of PCM for any applications are the energy storage capacity and the thermal conductivity.

The energy storage capacity of a PCM for a given application is given by the enthalpy variation between two temperatures and it involves the total energy (sensible and latent). Since the heat

Table 8
Chemical storage materials and reactions [49].

Compound	Reaction	Material energy density	Reaction temperature [°C]
Ammonia [50]	$NH_3 + \Delta H \leftrightarrow 1/2N_2 + 3/2H_2$	67 kJ/mol	400–500
Methane/water [51]	$CH_4 + H_2O \leftrightarrow CO + 3H_2$	n.a.	500–1000
Hydroxides, e.g. [51]	$Ca(OH_2) \leftrightarrow CaO + H_2O$	3 GJ/m^3	500
Calcium carbonate [51,52]	$CaCO_3 \leftrightarrow CaO + CO_2$	4.4 GJ/m^3	800–900
Iron carbonate [53]	$FeCO_3 \leftrightarrow FeO + CO_2$	2.6 GJ/m^3	180
Metal hydrides [51]	Metal $xH_2 \leftrightarrow$ metal $yH_2 + (x - y)H_2$	4 GJ/m^3	200–300
Metal oxides (Zn and Fe) [54]	e.g. 2-step water splitting using Fe_3O_4/FeO redox system	n.a.	2000–2500
Aluminium ore alumina [55]	n.a.	n.a.	2100–2300
Methanolation–demethanolation [56]	$CH_3OH \leftrightarrow CO + 2H_2$	n.a.	200–250
Magnesium oxide [57]	$MgO + H_2O \leftrightarrow Mg(OH)_2$	3.3 GJ/m^3	250–400

Table 9
Main characteristics of energy storage materials [25].

Thermal properties	Physical properties	Chemical properties	Economic properties
Phase change temperature fitted to application	Low density variation	Stability	Cheap and abundant
High change of enthalpy near temperature of use	High density	No phase separation	
High thermal conductivity in both liquid and solid phases (although not always)	Small or none undercooling	Compatibility with container materials	
		No toxic, no flammable, no pollutant	

transfer from a PCM storage system to a heat transfer fluid must be studied during charging and discharging processes, it is also necessary to study the evolution of thermal properties with temperature, which means that enthalpy vs. temperature curves are needed. Several authors have worked in the development of appropriate evaluation methodologies [64–72].

Analysis techniques used to study phase change are mainly conventional calorimetry, differential scanning calorimetry (DSC) and differential thermal analysis (DTA) [25]. Among the studies related to DSC, it is worth citing Flaherty [73] for characterization of hydrocarbons and natural waxes, Himran et al. [74] for characterization of alkanes and paraffin waxes, Giavarini and Pochetti [75] for characterization of petroleum products and Salyer et al. [76] for characterization of paraffins. DSC is the most used method for determining the storage capacity because is the most common commercial device, but there are several problems on

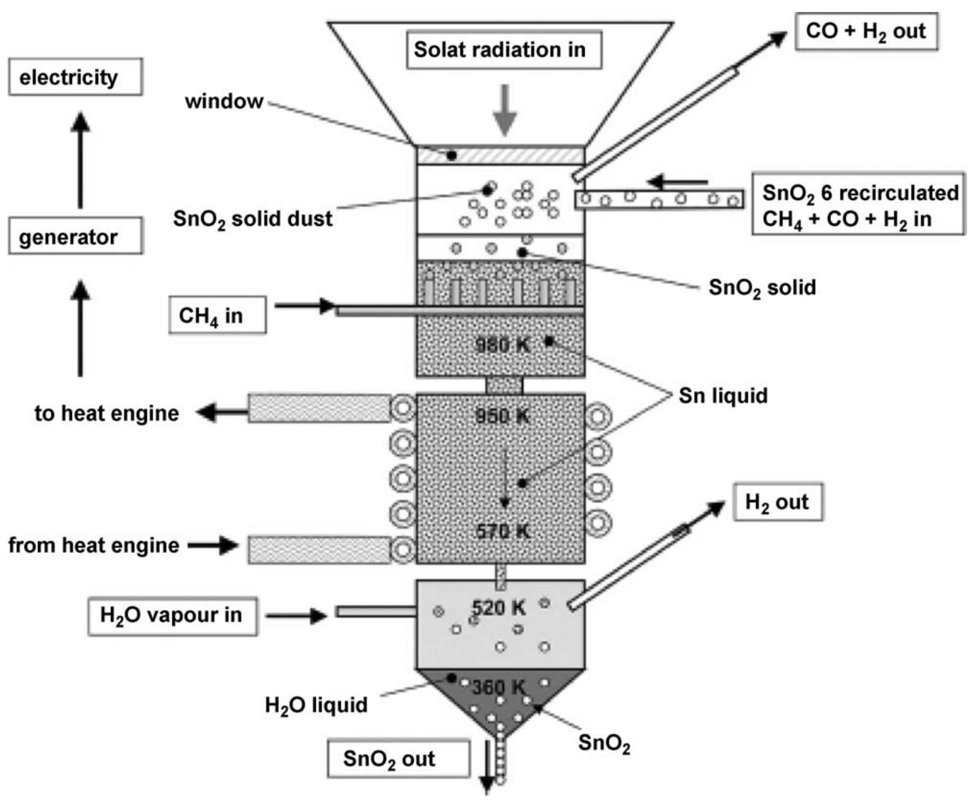


Fig. 11. Proposed schematic solar reactor for reaction (R3), in the upper part, heat recovery in the middle part, and hydrogen generation, in the lower part [21].

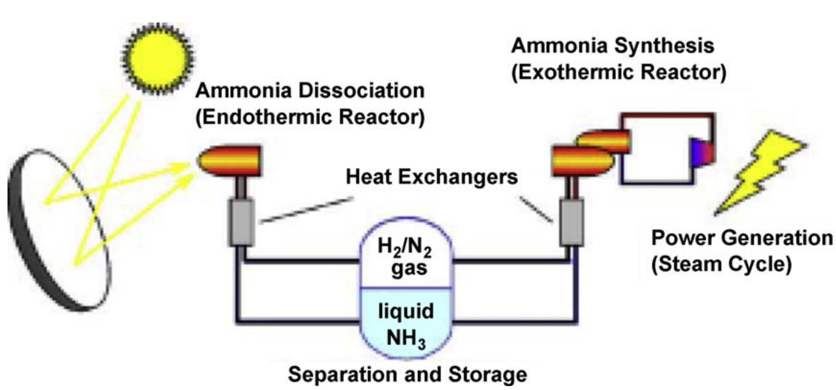


Fig. 12. Simplified scheme of operation of ammonia storage system [63].

using DSC for non pure, inorganic or low thermal conductivity substances [67,77–79] and as is mentioned in Gibbs and Hasnain [80], there is considerable uncertainty about the property values provided by manufacturers (who give values of pure substances). Some authors proposed the steps method [81] for solving some of those problems [78,82] or dynamic calorimetry to study the sensible and the latent heat separately [73,83–85].

The T-history method, proposed by Yinping and Yi [64] and improved by Marín et al. [65] is being implemented for several scientists to measure the enthalpy vs. temperature curves of organic and inorganic PCM during melting and solidification to study also other properties like subcooling, hysteresis and phase change temperature range [68,71,86].

Whereas the enthalpy vs. temperature curve determine the energy storage capacity of a PCM, the thermal conductivity is necessary to evaluate the rate of the heat transfer when a heat exchanger is designed. The most common method used is hot wire [87–90], nevertheless the temperature of the sample is measured with poor accuracy, in addition to the difficulty of measuring solid samples. A stationary method using parallel plates was found [91]. It solves the problem of accuracy on sample temperature measurement, but in liquid phase, convective movements deal with accuracy problems in the measurement. The Laser Flash method allows measuring in liquid and solid phase with accuracy in thermal diffusivity and temperature measurements of the sample. It is based on a laser pulse that comes into contact with one surface of the sample and the temperature evolution in the opposite surface is measured by an Infrared detector. The thickness must be perfectly known, so that a mathematical evaluation of the temperature evolution allows determining the thermal diffusivity of the sample. Then thermal conductivity is obtained by the Eq. (2).

$$\lambda = \rho \cdot c_p \cdot \alpha \tag{2}$$

where λ is the thermal conductivity [W/(m K)], ρ is the density [kg/m^3], c_p is the specific heat [J/(kg K)] and α thermal diffusivity [m^2/s]. It is used for measuring thermal conductivity of materials and composite materials for high temperature applications [92].

3.4. Corrosion in TES systems

Studies about corrosion in steel concluded that the impurities typically contained in commercial grades of alkali nitrates have relatively small effects in corrosion of stainless and carbon steels in molten salts prepared from these constituents [93–95].

Thermal cycling generally aggravates high temperature oxidation, but the degree to which a particular material may be affected in any given environment is difficult to predict. A test of resistance of stainless steels (used to made the hot tank in two tanks storage system) during thermal cycling in molten salts studied the corrosion of three stainless steel samples with four different mixtures of nitrate salts [96,97]. In this study, stainless steel coupons were immersed in crucibles that contained about 10 kg of the nitrate mixtures. The cycling period was established in 7.5 h at the maximum temperature and 0.5 h cooling in ambient air, for a total cycle time of 8 h. This schedule allowed three cycles per day, for a total of 500 thermal cycles during 4000 h of operation.

In order to be able to compare the corrosion levels in every case, three more samples were tested under an isothermal immersion of molten nitrate salts.

The conclusion of this test was that thermal cycling increased the corrosion rates of three stainless steel samples, compared to isothermal immersion in the molten salt, but the increase was moderate, between 25% and 50%, depending on the chloride content of the molten salt [96–97].

In applications where exposure to nitrate salts can be limited to 400 °C or less, the use of carbon steels may be considered. The corrosion in carbon steels (used to make the cold tank) was studied under the point of view of effect of dissolved impurities, such as chloride and sulphate, on corrosion as compared to pure nitrate melts. Results of short-term corrosion tests of carbon steels in molten salts show that the corrosion of mild steel at 400 °C increased approximately as the logarithm of the chloride concentration [98]. At 0.6 wt.% NaCl, the corrosion rate increased by a factor of about three compared to a chloride-free melt, during an 8 h test. Corrosion rates increased by about a factor of four during a 25 h test, when the chloride concentration was 0.7 wt.% compared to a chloride-free melt. The effect of dissolved sulphate in nitrate melts on corrosion of mild steel results in corrosion rates increased by 20% when 7.5 wt.% Na_2SO_4 was added to the pure molten salt [99].

Long-term experiments have been conducted to verify the corrosion resistance of carbon steel in commercial-purity nitrate salts. The temperature of operation for the experiments was 316 °C, and the result was that the samples exposed to the high-purity molten salts corroded slowly at this temperature, losing about 1–3 mg/m^2 after 4000 h of tests. Weight losses increased as the chloride level increased. The samples exposed to the ternary nitrate salt corroded vary slowly, losing only 0.3 mg/cm^2 after 4000 h of test.

On the other hand, in order to be sure of results of the report previous to start-up, after the Solar Two plant finished its operation, the corrosion in the tanks was tested. The interior surface of the tanks was exposed to the nitrate salts continuously at or near their operating temperatures during all plant operating time (over 30,000 h). Samples were removed from areas of the tank walls and were examined for corrosion penetration, surface contamination and oxide growth. Analyses showed that corrosion occurred at an acceptably low rate [93]. Corrosion after more than 30,000 h of exposure time was minimal. Concerning to cold tank, there were not unusual features with respect to oxide structure or oxidation products on carbon steel used to construct it. For the hot tank, the only singular observation was the presence of oxide films of only minimal thickness.

4. Modelling of high temperature storage systems

In order to have simulation, analysis and design tools, it is relevant to gather information about thermal energy storage modelling for such materials at high temperature operation. In fact, authors like Arahal et al. [100] point out that storage tanks and phase change slurries (PCS) modelling have not received such attention until recently.

4.1. Sensible heat storage materials

4.1.1. Solid

Laing et al. [18] presented a numerical tool for simulation of the transient performance of storage systems. The simulation environment is "StorageTech-Thermo", where the storage is described by physical models, allowing also the dynamic simulation of the system. Comparing with experimental data (Fig. 13) they show very good results for charging and some deviations for discharging at low temperatures.

Tamme et al. [46] implemented a simulation tool for the analysis of the transient performance of solid media sensible heat storage systems. In their results they show the influence of various parameters describing the storage system. They point out that while the effects of the storage material properties are limited, the selected geometry of the storage system is important. In this work, they explain the model used by Laing et al. [18].

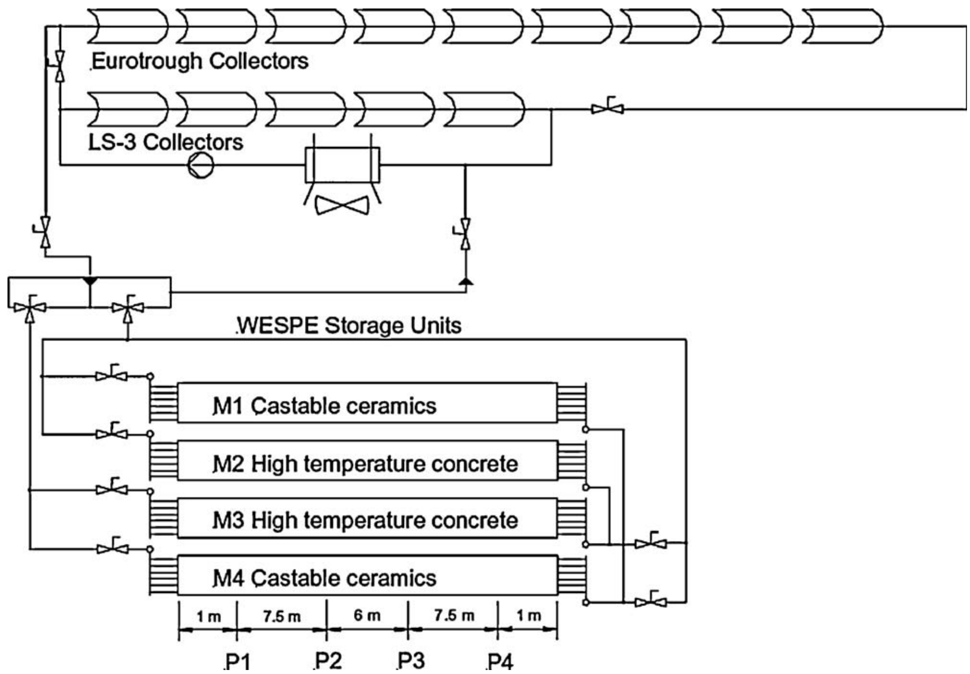


Fig. 13. Integration of storage modules into parabolic trough test loop at PSA (Plataforma Solar de Almería) [18].

The tube and the storage material are discretized in the axial direction, the storage material is also discretized in radial direction (Fig. 14). They present some sensitivity analysis using a differential storage element.

Laing et al. [101] presented a finite element method (FEM) analysis for a segment of a storage pipe with concrete (without fins and with axial fins) with the same tube spacing (Fig. 15). Finite element method analyses were performed on top of the basic configuration for axial fins, orthogonal reinforcement grids, and for radial fins, all with the same spacing as the distance between tubes.

Rafidi and Blasiak [102] developed a two-dimensional simulation model to numerically determine the dynamic temperature and velocity profiles of gases and solid heat-storing materials in a composite material honeycomb regenerator (Fig. 16). Authors presented experimental data to validate the model.

4.1.2. Liquid

Herrmann et al. [7] used a program called "PCTrough" to determine the electricity production from solar power plant with and without storage. The storage model also considered heat losses of the cold and hot storage tanks. In this work, the HTF also served as storage medium.

Maveety and Razani [103] presented a two-dimensional numerical investigation of a thermal storage system and its corresponding subsystem in order to exploit second-law char-

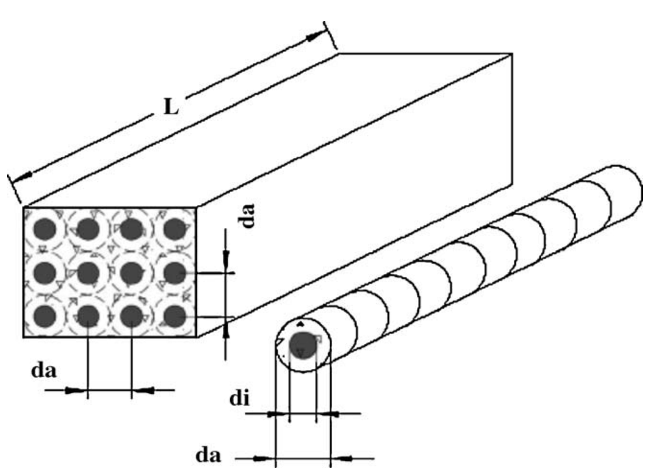


Fig. 14. Physical model for the storage unit and parameters describing the geometry [46].

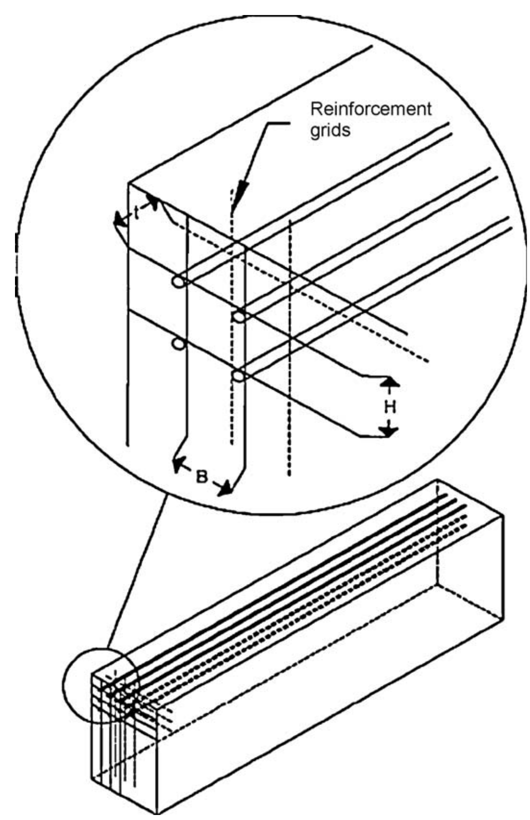


Fig. 15. Orthogonal reinforcement grids (to enhance heat transfer in the storage structure) analysed with the finite element method [101].

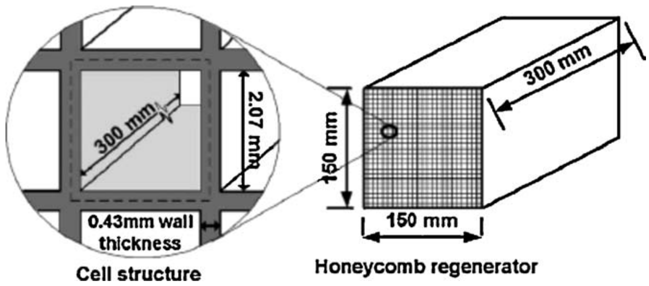


Fig. 16. Honeycomb regenerator and dimensions of solid material and flow paths [102].

acteristics. They developed a transient analysis of a cylindrical thermal storage system for which the working fluid is a sodium–potassium alloy (NaK). Due to its properties, NaK is used as a refrigerant fluid in applications as core reactor cooling or heat pipes.

The explicit finite difference technique was used in this work. Spatial approximation was accurate to the second order through use of the central-difference scheme. The temporal approximation was accurate to first-order since a forward-difference scheme was implemented.

Arahal et al. [100] presented a model of the thermal storage tank that was derived using the Simultaneous Perturbation Stochastic Approximation (SPSA) technique to adjust the parameters of a serial grey-box model structure (parameters were obtained from data using the SPSA optimization algorithm). The model to be used in hierarchical control schemes was also proposed by the authors. The model structure for the thermal storage tank corresponded to a discrete-time set of first order equations. The model was validated with experimental data (Fig. 17).

Vaivudh et al. [104] developed a mathematical model of non-steady state heat exchanger. They used a cylindrical sensible storage tank (Fig. 18). A heat exchanger of thermal energy storage was used for separating two fluids, storage medium and heat transfer fluid. Two types of set up were evaluated: vertical pipe and helical coiled pipe. They show an error lower than 10% between experimental data and simulated results.

4.1.3. Packed bed

Mawire and McPherson [105,106] used the energy balance equations to model the solar energy capture system and the thermal energy storage system of a proposed indirect solar cooker. An oil–pebble bed was used as the TES material (Fig. 19). The model was a modified version of the Schumann model with some assumptions. Runge–Kutta numerical integration method was used to predict the outlet temperature of the absorber coil. Energy and exergy analyses were done in this work. They employed "Simulink" of 6.5 "Matlab" version.

Mawire and McPherson [107] also developed a control model to enable simulation of a feedforward internal model control (IMC) structure. Using a Simulink block model, the simulation results revealed that a feedforward IMC structure performs better than a feedforward structure.

Fricker [108], using a special computer program, described thermodynamically different core geometries and materials to be used in a packed bed system. Storage temperature distributions were presented in this work (Fig. 20).

Pacheco et al. [109] simulated the thermal behaviour of the tank by the Schumann equations, which described the heat transfer between the fluid and a packed bed (Fig. 21). In this research, they modelled the performance and estimated the economics of a thermocline system. The system was one-dimensional, finite

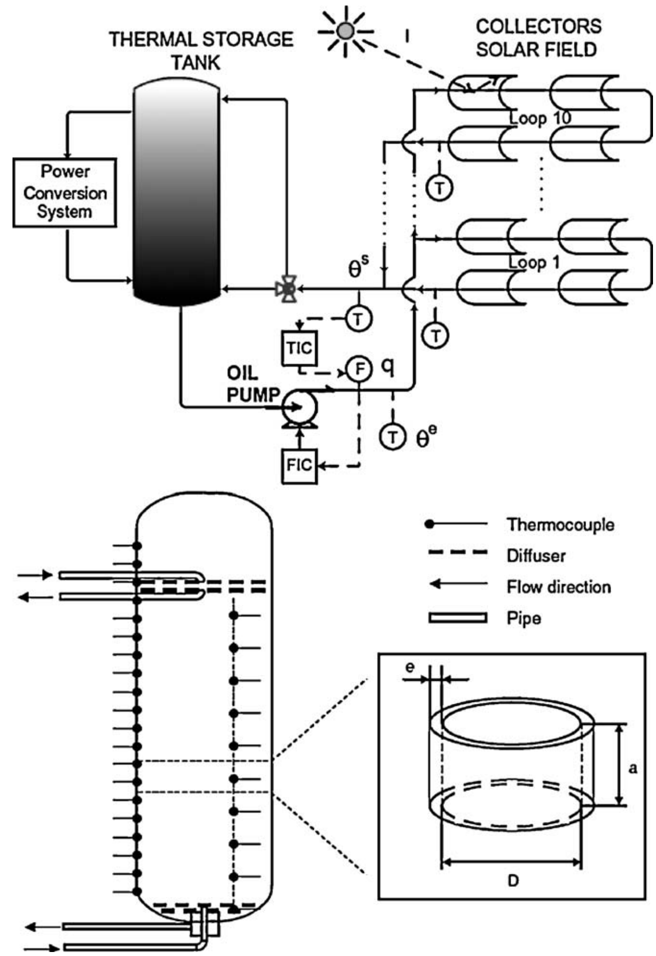


Fig. 17. Top: schematic layout of the small solar power systems (SPSS) plant at the PSA. Bottom: diagram of the tank. The inset shows a generic discrete control volume used for modelling [100].

difference representation. It used the modified Euler's method to correct the predicted fluid and bed temperatures. All the code was written in "Visual Basic" using "Microsoft Excel" and ran as a macro. They validate the model with experimental data and they present some screening studies.

4.2. Latent heat storage materials

4.2.1. Cylinder-tube geometry

The cylinder-tube geometry is the more widely studied. He and Zhang [110] solved numerically a mathematical model describing the unsteady freezing problem coupled with forced convection. The method of finite difference was used to solve the equations. Center-difference and full implicit scheme was useful in this work. Three stages treatment leaded to solution of phase change process equations. In their results they marked the importance of PCM thickness. Their numerical results were compared with experimental values (Fig. 22).

Buschle et al. [38] described the model used in Do Couto et al. [39]. They employed the "Modelica" software. For the simulation, the storage tube was discretized into control volumes in the axial direction (Fig. 23). The PCM around the storage tube elements was further discretized in the radial direction. Three ways to calculate the enthalpy in the "Modelica.Media" models were compared. The first method was the linear interpolation using If-, Elseif- and Else-clauses; the second method was the usage of the arc tangent function; and the third method was the usage of the error function.

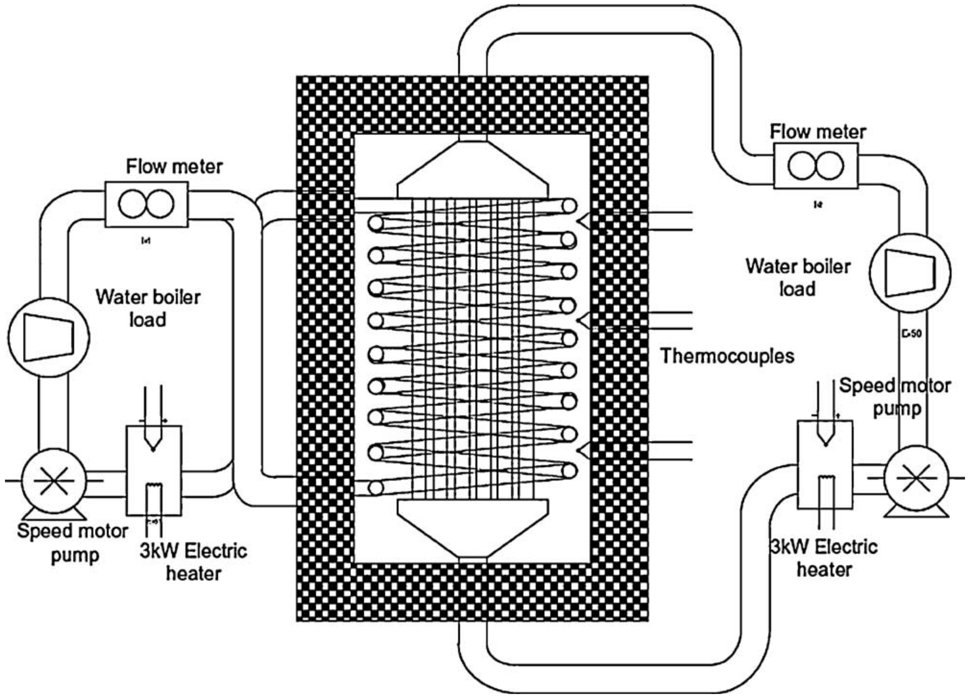


Fig. 18. The system of thermal energy storage with the vertical straight pipe and the helical coiled pipe inside the storage tank [104].

Michels and Pitz-Paal [36] presented a numerical model to simulate different cascaded latent heat storage (CLHS) configurations. "Dymola/Modelica" was used to conduct the simulation using the standard library Tech-Thermo. They used some assumptions to simplify: the PCM was considered as a lumped mass with a uniform temperature throughout. In this work natural convection was also considered. With their simulated results they presented experimental data to validate the model (Fig. 24).

Zhen-Xiang and Mujumdar [111] developed a finite element model to simulate the cyclic thermal process involved as a result of alternating melting and freezing processes. The physical module consists of a tube which is surrounded by an external coaxial cylinder made up of several segments of different PCMs with different melting points (Fig. 25). Semi-discrete equations using standard Galerkin finite element method was used. In their numerical results they indicate that the heat transfer rates can be greatly enhanced using multiple PCM as compared with a single PCM. They also applied this model to space-based activities [112].

Cui et al. [113] analysed the energy transfer of the heat receiver cavity (Fig. 26). They developed a heat balance model of the solar heat receiver, a cavity radiation mathematical model and a working fluid tube heat transfer model. The enthalpy formulation

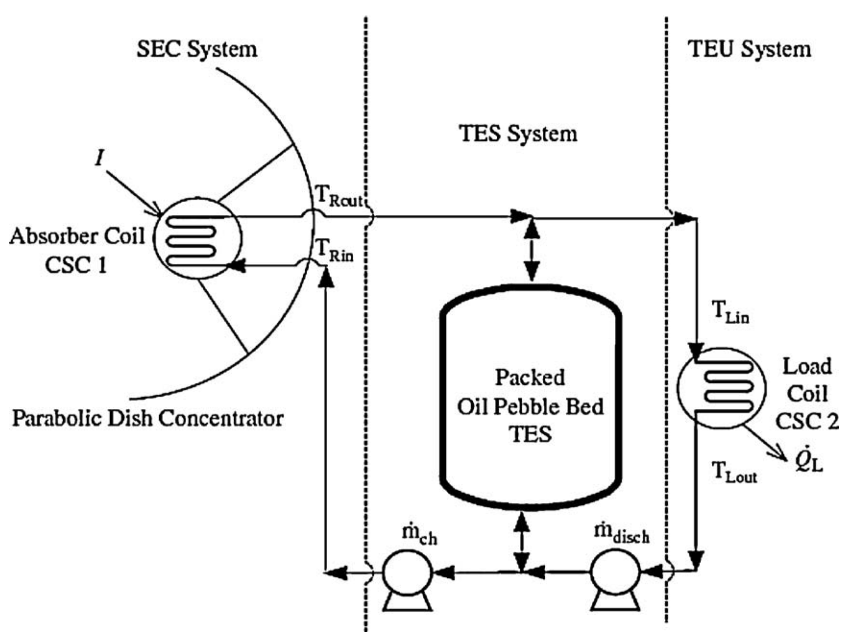


Fig. 19. Conceptual diagram of an indirect solar TES and cooking system [105].

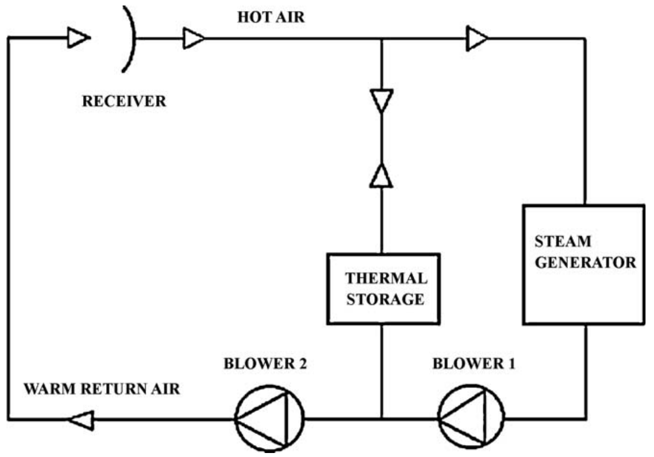


Fig. 20. Main components of the atmospheric air system studied by Fricker [108].

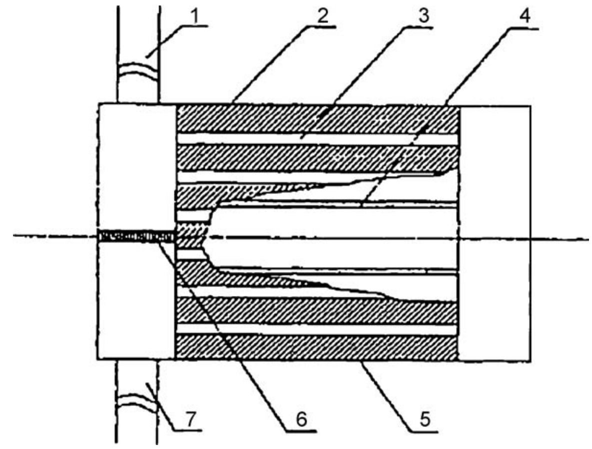


Fig. 22. Main outlets of the exchanger. (1) Tube for gas entrance; (2) PCM; (3) tube for heat transfer; (4) electrical heater; (5) shell; (6) baffle-board; (7) tube for gas exit [110].

of the heat transfer equation was used for the tubes. The system was studied as a three-dimensional cylindrical coordinate using the finite volume method with a simple explicit scheme. They conclude that the design of the working fluid tube needs to be further improved in order to increase the liquid PCM fraction and reduce both the gas outlet temperature variation and the system mass.

Cui et al. [114], based on enthalpy method, developed a numerical model of the unit heat exchanger tube (Fig. 27). The model considered PCM solid or liquid heat resistance and the influence of the void. The enthalpy method energy equation was used with some assumptions: phase change takes place at a distinct temperature. Conservation of the energy equation was expressed in three-dimensional cylindrical coordinate. The comparison with experimental results showed higher values of the simulated results.

Charxiu and Wujun [115] used the phase change package of ''Fluent'' (enthalpy-porosity technique) to perform the numerical simulations. Transient two dimensional heat conduction problems were solved using the Fluent 6.2 software when heat was extracted from the PCM during the discharging process. They pointed out that adding aluminium foils was an efficient way to enhance the heat transfer (Fig. 28). Some parametric studies were presented.

Yimer and Adami [116] developed a two dimensional transient analytical model based on the enthalpy method (Fig. 29). They presented a dimensionless analysis. Two dimensional finite difference representation was used: radial and angular variations, and radial and axial variations. The Gauss–Seidel iterative method with successive over-relaxation (SOR) was used to solve the non-linear simultaneous difference equations. Some parametric studies were shown also.

Hoshi et al. [117] developed a double tube latent heat thermal energy storage model system (Fig. 30). They presented a classification of high temperature PCM according to heat capacity, phase change temperature, thermal conductivity, and cost. At the same time they presented a model with some assumptions: PCM constant properties, and no natural convection in PCM. In this work, the successive over-relaxation method was used.

Morisson et al. [40] reported a detailed model of heat transfer and fluid flow for numerical simulation of latent heat storage unit which takes into account the solid/liquid and water/vapour phase change processes occurring simultaneously in the PCM and heat transfer fluid with appropriate coupling between them. A typical storage block was composed of parallel tubes for the water/steam

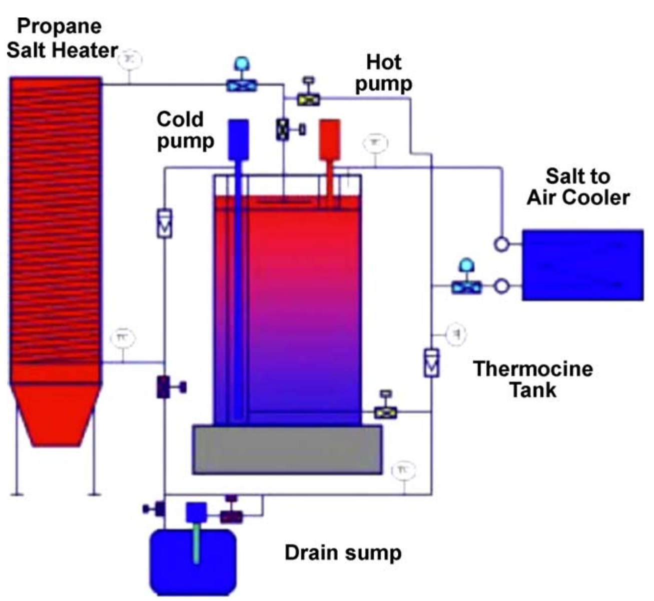


Fig. 21. Schematic of the 2.3 MWh thermocline flow loop [119].

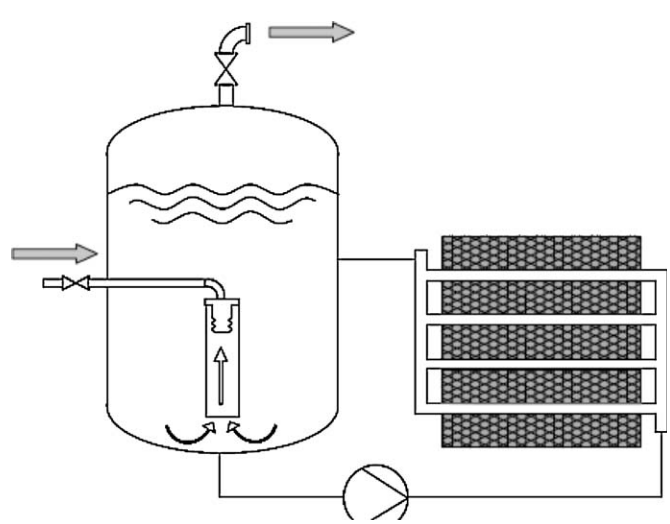


Fig. 23. PCM enhanced steam accumulator [38].

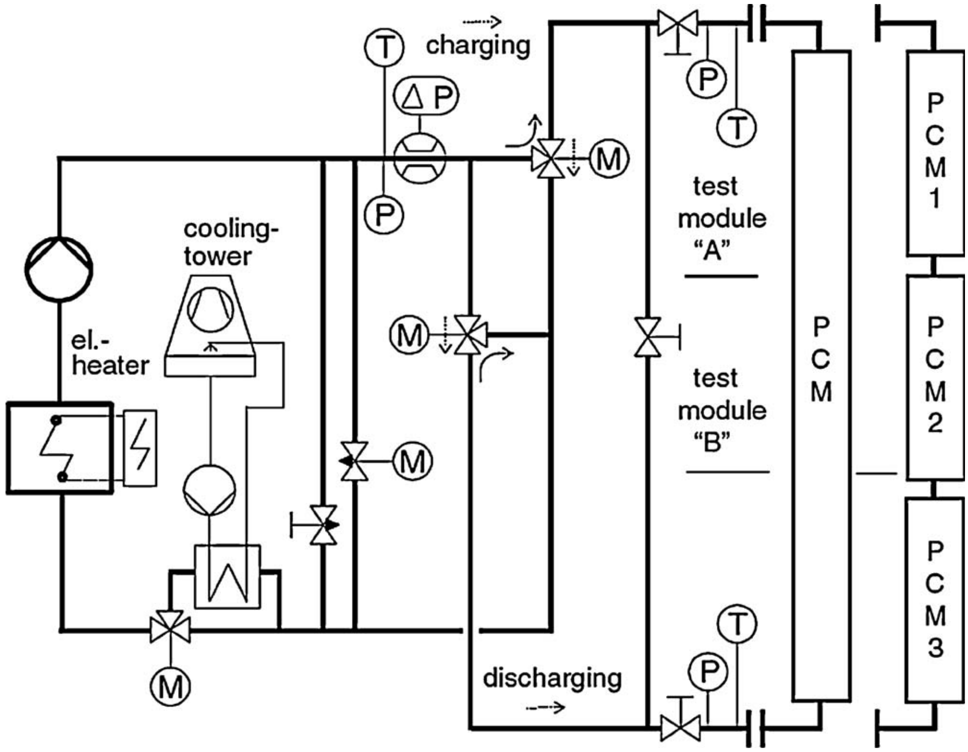


Fig. 24. Simplified flow diagram of the thermal oil test facility [36].

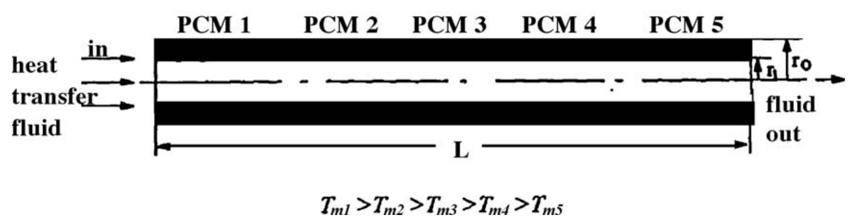


Fig. 25. Physical model of the tube-segmented PCM cylinders structure [111].

passing through the unit (Fig. 31). The tubes were embedded in the storage material. The assumptions used were: heat transfer within PCM is controlled by conduction; convection plays a negligible role taking into account the strong viscosity of salt in the liquid state and of its encapsulation on the level of the pores of micrometric size of the graphite matrix. They first run a simplified model in order to get some parameters required to start running the detailed model.

Cui et al. [43] presented a model composed of three different phase change temperature materials together with the corre-

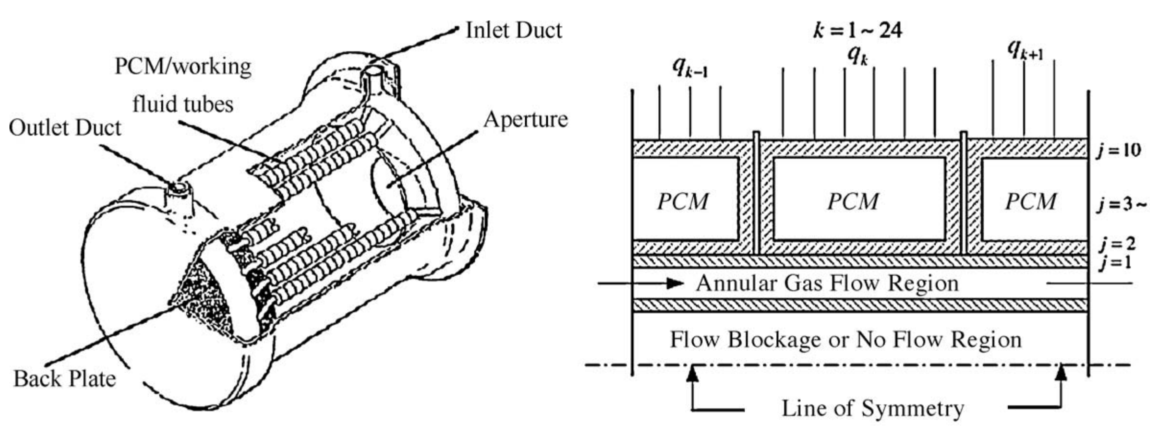


Fig. 26. Left: solar heat receivers. Right: schematic of encapsulated PCM tube configuration with annular gas flow [113].

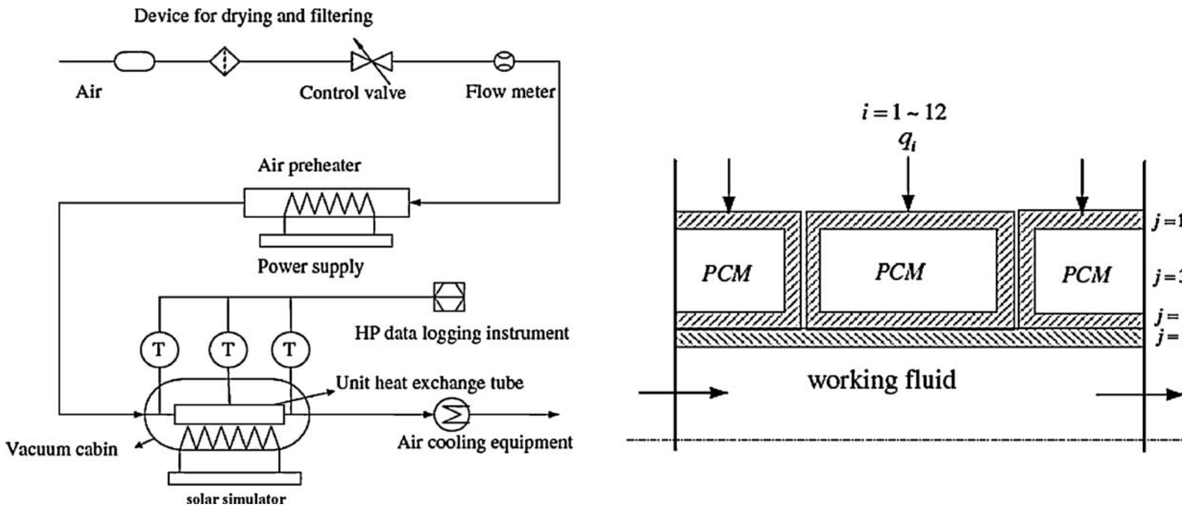


Fig. 27. Left: scheme of experiment system. Right: schematic of PCM tube configuration [114].

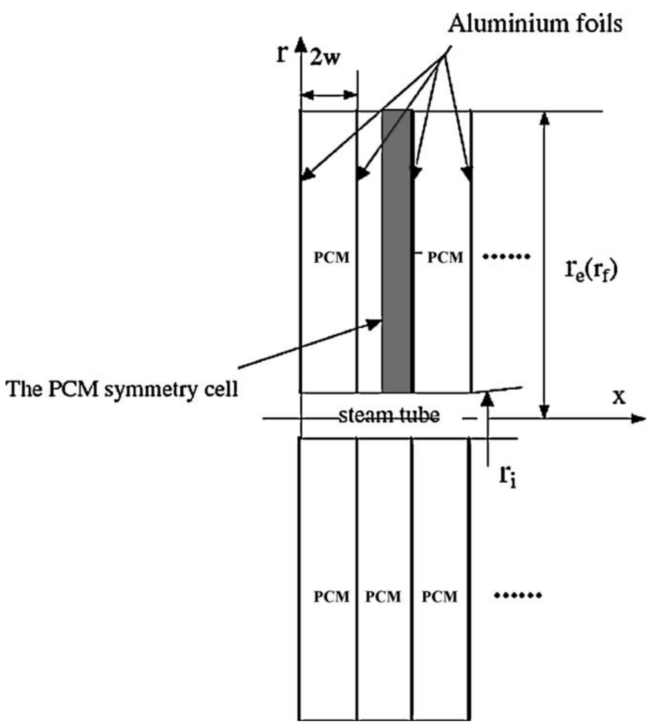


Fig. 28. Layout of the problem studied by Chaxiu and Wujun [115].

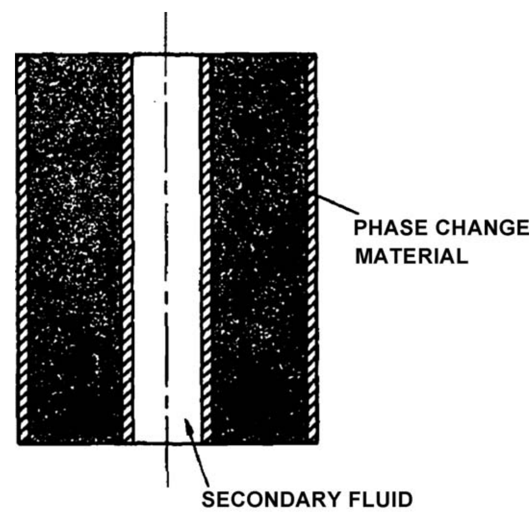


Fig. 29. Configuration for the 2D system [116].

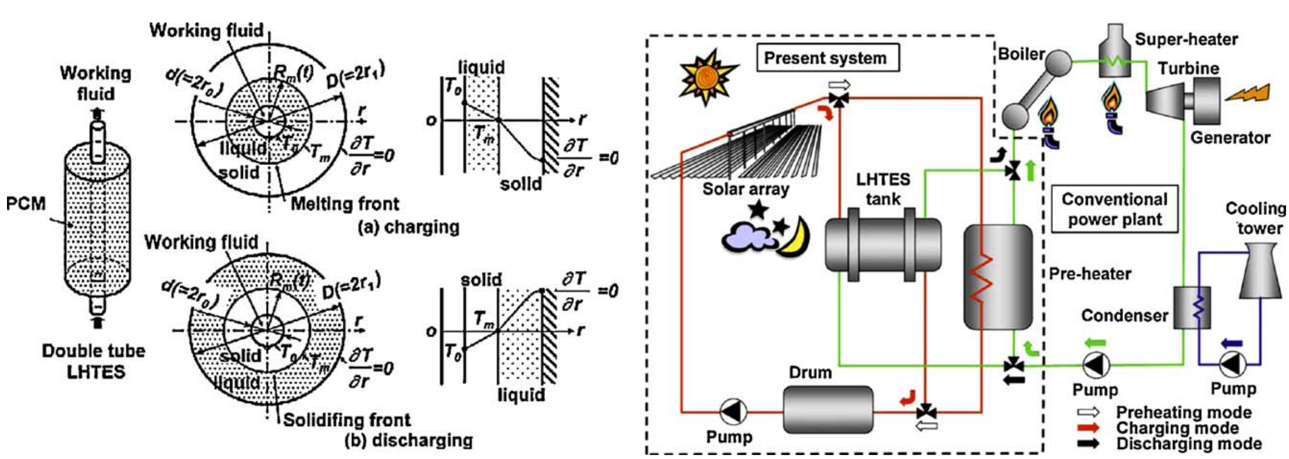


Fig. 30. Left: schematic of PCM tube configuration. Right: layout of the plant [117].

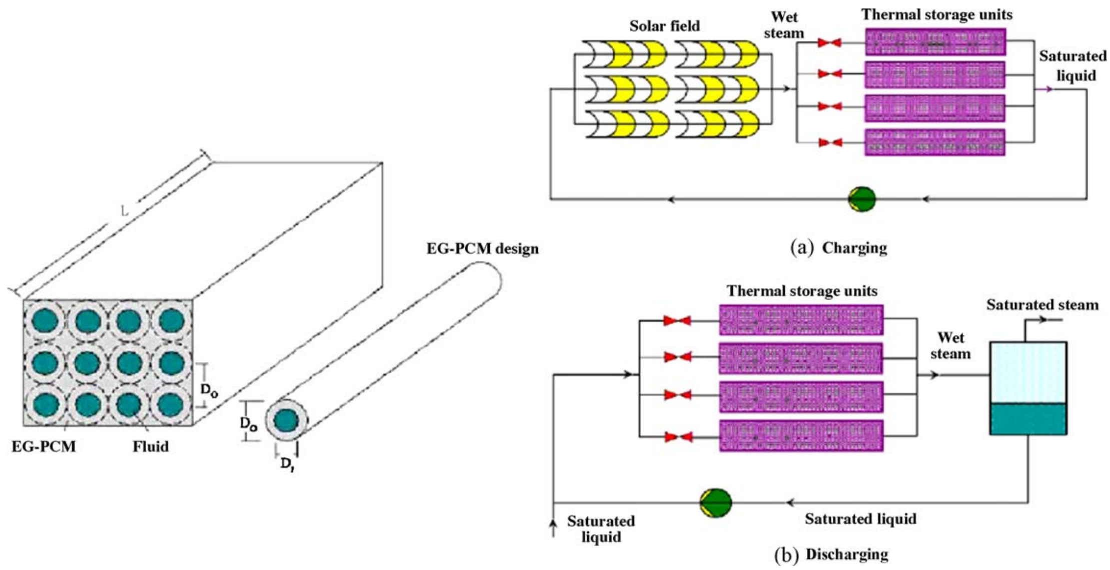


Fig. 31. Left: configuration of a single storage block. Right: simplified control schemes during charging and discharging modes of operation [40].

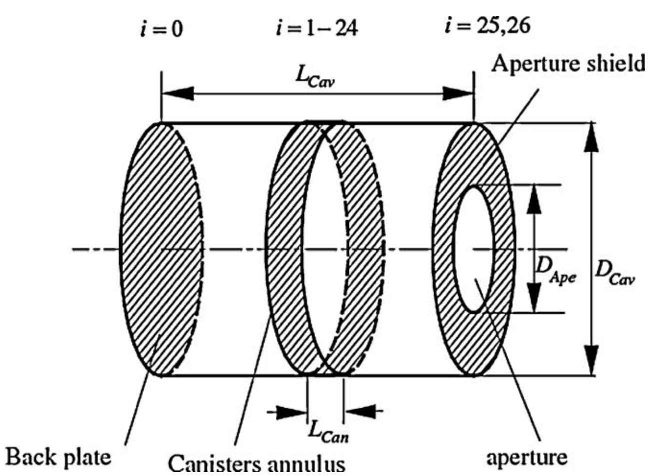


Fig. 32. The radiation model of the heat receiver cavity [43].

sponding physical model (Fig. 32). They found that, using multiple PCM compared with a single PCM, it not only can enhance the energy rate, but also can decrease the fluctuation of the gas exit temperature greatly. The results show that it is possible to increase the receiver performance and reduce the weight of heat receiver.

Lafdi et al. [118] developed a model to study carbon foams saturated with PCM to use as thermal storage material. The numerical model was based on a volume averaging technique while a finite volume method was used to discretize the heat diffusion equation. A line-by-line solver based on tri-diagonal matrix algorithm was used to iteratively solve the algebraic discretization equations. 2-D general coordinates were used (Fig. 33). A mathematical formulation of the governing equations on non-orthogonal curvilinear system was employed. The standard SIMPLE (Semi-Implicit Method for Pressure Linked Equations) algorithm was used to solve the coupled continuity and momentum equations. The model was validated with data from Khillarkar et al. [119].

4.2.2. Packed bed

Yagi and Akiyama [120] studied a single sphere and a packed bed (Fig. 34). A model for a single spherical capsule was developed and a heat transfer simulation was also conducted for a packed bed process of spherical capsules. Enthalpy method with some assumptions was used in this work; convection and radiation in the surface are considered; fully implicit scheme based on control volume (with SOR method) was used. The gas flow in a packed bed was studied with the SIMPLE method. The model results were compared with experimental data showing some differences.

Jalalzadeh-Azar [121] developed a packed bed computational model that validated experimentally. In this work, second-law thermodynamic analyses along with material stability tests were employed as criteria for the assessment of these materials (PCM and sensible-heat pellets).

4.3. Chemical heat storage materials

Sakurai et al. [122] used the "ASPEN-PLUS" for the evaluation of the thermochemical process for hydrogen production. The process has five compounds and is carried out in four steps:

$$CaBr_2(s) + H_2O(g) \rightarrow CaO(s) + 2HBr(g) \quad (R5)$$

$$CaO(s) + Br_2(g) \rightarrow CaBr_2(s) + 1/2O_2(g) \quad (R6)$$

$$Fe_3O_4(s) + 8HBr(g) \rightarrow 3FeBr_2(s) + 4H_2O(g) + Br_2(g) \quad (R7)$$

$$3FeBr_2(s) + 4H_2O(g) \rightarrow Fe_3O_4(s) + 6HBr(g) + H_2(g) \quad (R8)$$

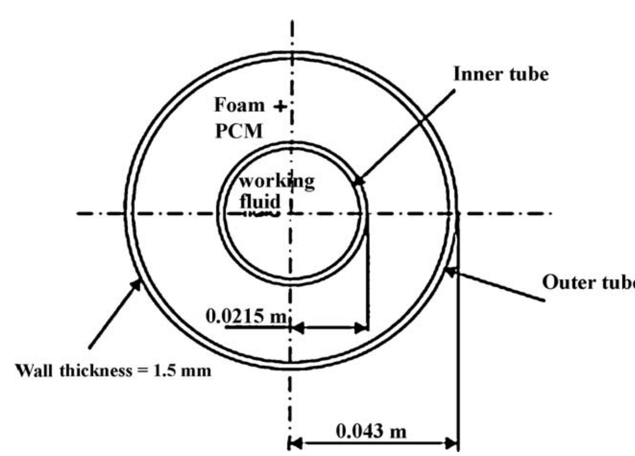


Fig. 33. Computational model for space applications [118].

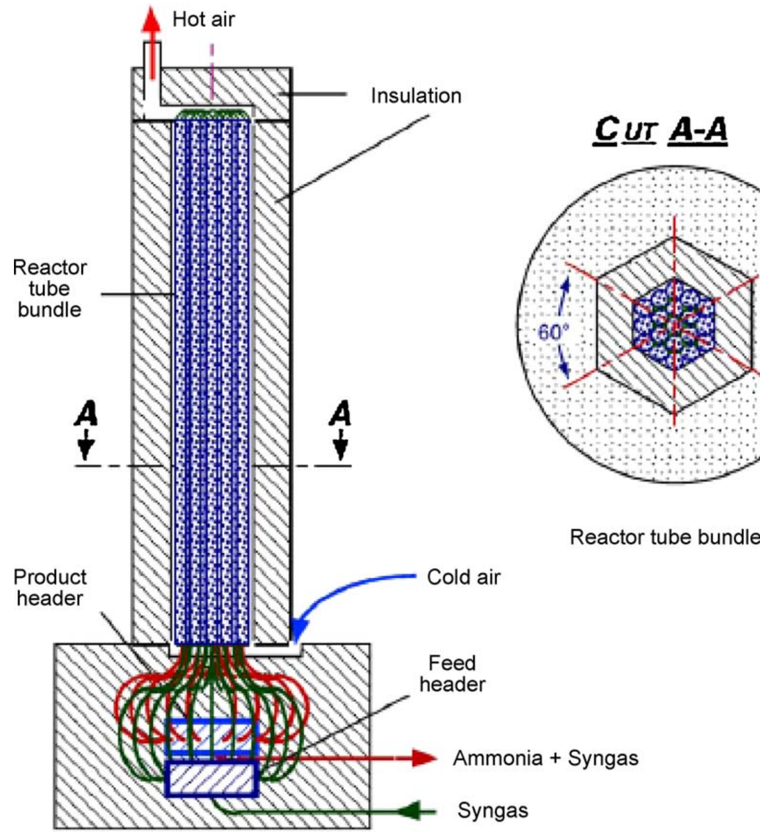


Fig. 34. Experimental apparatus for heat storage and heat release in a single capsule including PCM [120].

In their work the thermal storage requirements were calculated and an exergy analysis was also done. They found that the overall thermal efficiency is 49.5%, the exergetic efficiency is 52.9% and the process can be realized using conventional materials.

Kreetz and Lovegrove [60] developed a tubular packed-bed catalytic ammonia reactor with a two-dimensional pseudo-homogeneous model. The model produced a numerical solution heavily depending on semi-empirical correlations for mass and heat transfer parameters. They used it later [123] presenting an exergy analysis of their system (Fig. 35). The model was a "Fortran" program modified: simultaneous reaction and heat and mass transfer mechanisms were taken into consideration. The successful

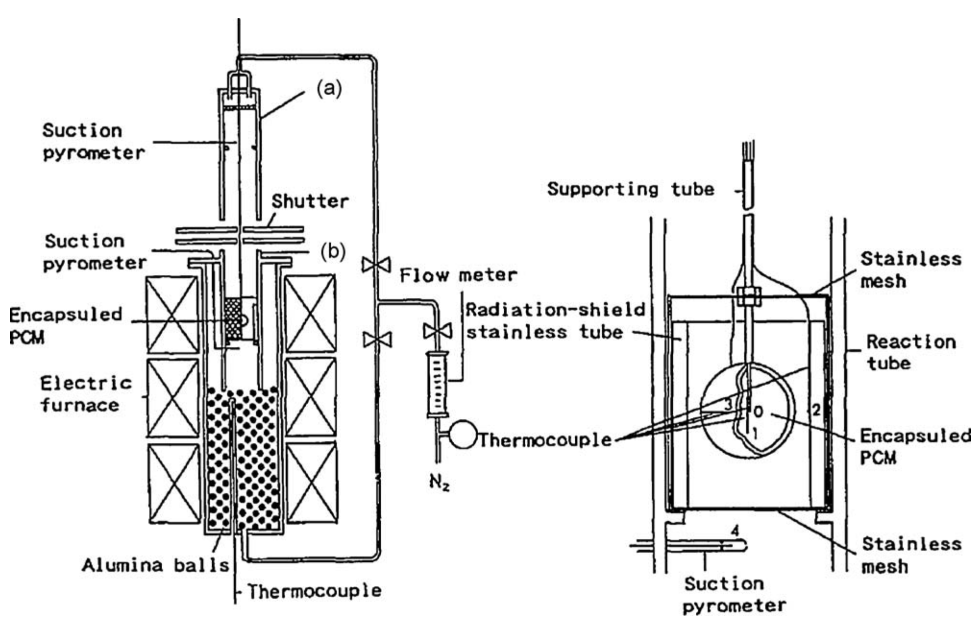


Fig. 35. Ammonia synthesis heat recovery reactor [123].

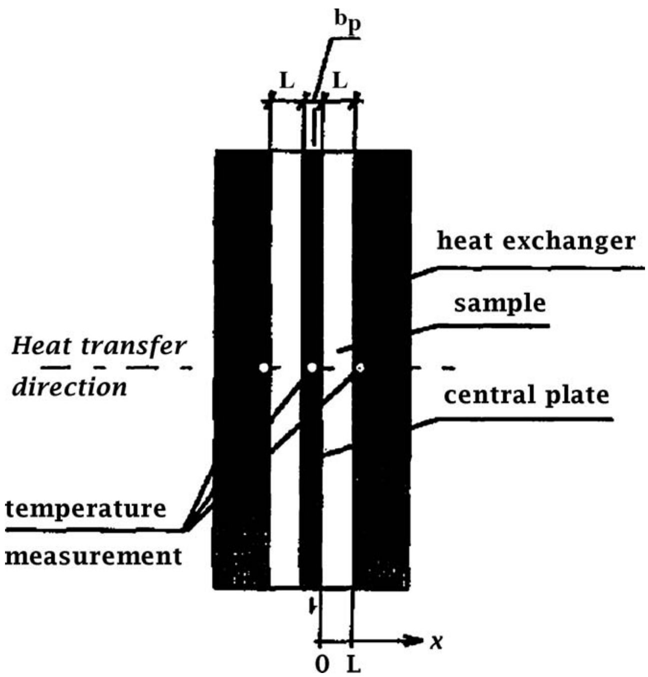


Fig. 36. Experimental configuration of the apparatus used to determine the thermal conductivity of thermoplastics (the apparatus has been studied to deal with the conditions of polymer injection in a mould) [124].

experimental investigation (laboratory scale) enabled the validity of a numerical reactor model previously used with success for ammonia dissociation reactors and confirmed for ammonia synthesis as well. Their results showed a good agreement between the numerical model and the experimental results (achieved when some parameters were given: measured inlet reaction extend, external reactor wall temperature profile and an adjustment of intrinsic rate parameters).

4.4. Miscellaneous

Jurkowski et al. [124] developed a model to determine thermal conductivity of thermoplastics over a wide range of temperature, involving a phase change (Fig. 36). The model was based on the inverse analysis of non-linear transient heat conduction, but in this work temperature measurements were recorded at the boundary of a thin sample. Finite differences and a Crank–Nicolson scheme were used in this work. Thermal contact resistance (TCR) resulting from the external location of the sensors is considered in the model. The convergence of the iterative optimization algorithm was improved and the evaluation of errors on the estimated parameters due to measurement errors and model errors was studied.

Wang et al. [125] studied a heater (Fig. 37). They showed first calculations for heat discharge rate and heat storage ratio: lumped capacitance method was adopted for the heat transfer in the PCM because Bi <0.1. They pointed out that further modelling and optimization was needed to be done in the future.

Cummer and Brown [126] studied a ballast gasification tubes system. They proposed the remodelling of the cooling curves for the ballasting system as they were not well predicted during phase change of the lithium fluoride (Fig. 38). A reformulated model, known as the Receding Interface (RI) model, postulated the existence of a receding liquid phase within the ballast tubes as they cool, which progressively decreased the rate of heat transfer from the tubes. The previous formulation was the Lumped Capacitance model (valid if Bi <0.1). The new one was the Receding Interface model that had some assumptions: 1D radial heat transfer, and phase change at constant temperature. This model was a fourth-order Runge–Kutta method to integrate the equations and was written in the "C++" programming language. Some sensitivity analyses were done. They presented experimental validation with the numerical results.

Notter and Hahne [127] developed several thermal expansion models to study polycrystalline salt-ceramics when used as high temperature storage materials. They also validated their model with copper lead alloys, showing differences with experimental lower than 7%.

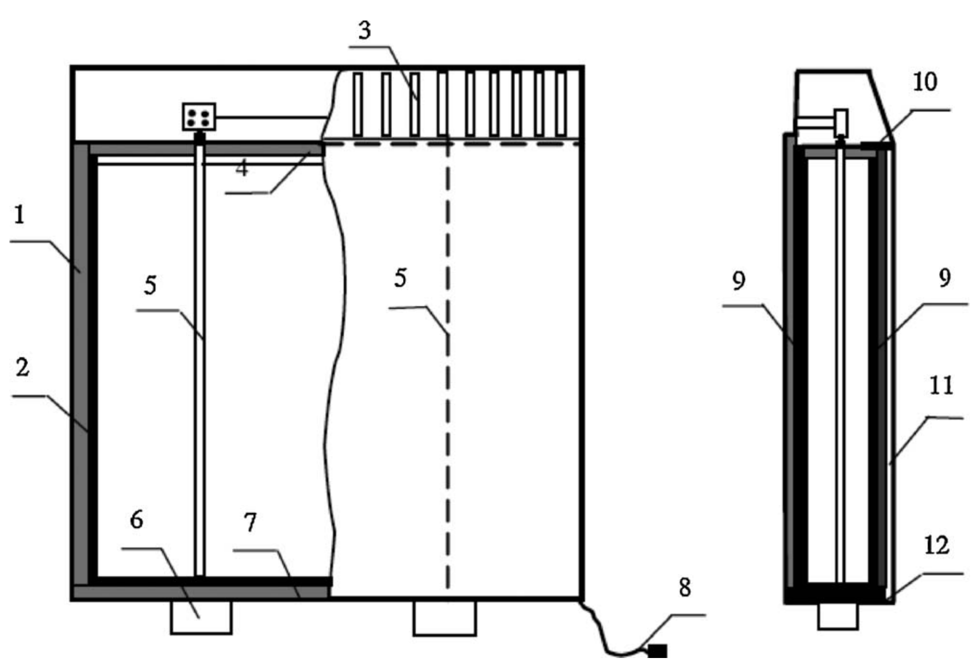


Fig. 37. Scheme of structure of high temperature phase change storage heater [125].

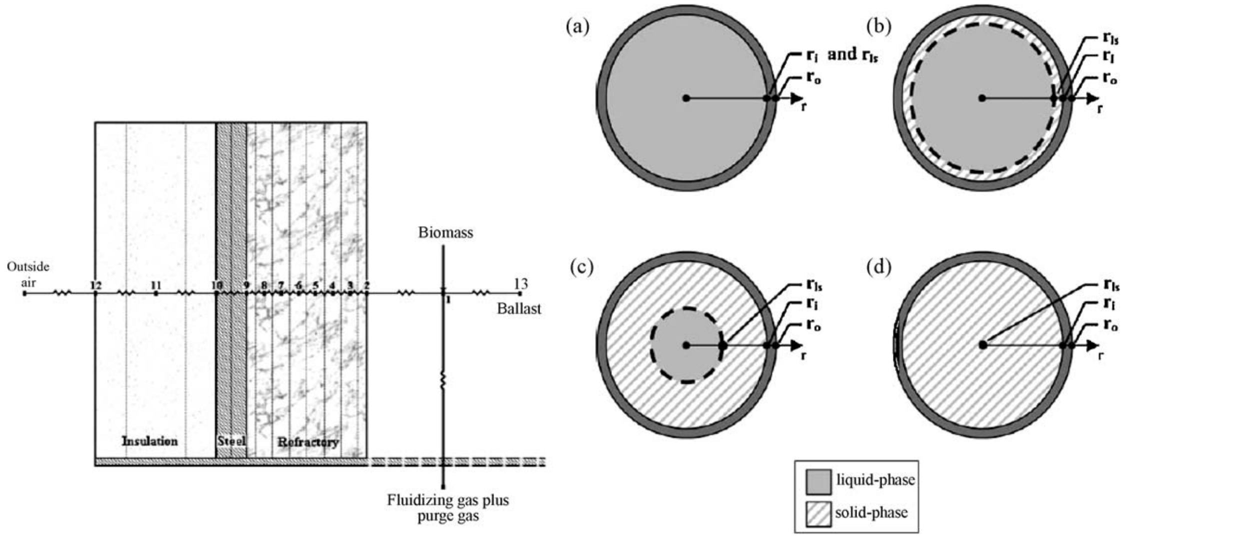


Fig. 38. Left: ballasted gasification nodal network. Right: illustration of RI model applied to ballast tubes [126].

5. Conclusions

This paper analyses the information available in the open literature regarding high temperature thermal storage for power generation, with the focus on the classification of storage system concepts; the description of the materials used in these different storage concepts; as well as the review of the physical models used to simulate such systems. The following conclusions can be drawn:

1. The development of an efficient and cost-effective thermal storage system is crucial for the future development of concentrated solar power, as it allows a better dispatchability of the power plant and a higher power capacity factor.
2. The requirements for a thermal storage system are: high energy density in the storage material (storage capacity); good heat transfer between heat transfer fluid (HTF) and the storage medium; mechanical and chemical stability of storage material; compatibility between HTF, heat exchanger and/or storage medium (safety); complete reversibility of a number of charging/discharging cycles (lifetime); low thermal losses; ease of control; operation strategy; maximum load; nominal temperature and specific enthalpy drop in load; and integration into the power plant.
3. According to the storage media, storage systems are classified as sensible heat storage, latent heat storage and chemical heat storage. Only the sensible heat ones have been actually used in real solar power plants, although both PCM and chemical storage offer some advantages and are the target storage technologies for future plants.
4. According to the storage concept, the systems can be classified as active and passive. The first ones involve forced convection heat transfer into the storage material, either directly with the storage media (direct systems) or indirectly, being the heat transfer fluid and the storage medium different substances. In passive systems the thermal storage medium itself does not circulate.
5. Most of the energy storage concepts used in real solar power plants are active systems. These systems include one direct system: the two tanks direct system using molten salts as storage media and heat transfer fluid; and two indirect system: the two tanks indirect system using molten salts as storage media only and other fluid as heat transfer fluid, normally oil, and the single tank direct system (also called thermocline system). Passive systems such as the solid media sensible heat store or the PCM latent heat system have been investigated in several studies and projects.
6. All the storage materials used currently in solar power plants are based on liquid sensible heat storage. Two molten salts are the most used ones: the so-called solar salt is a binary salt consisting of 60% $NaNO_3$ and 40% KNO_3, and the salt sold commercially as HitecXL, which is a ternary salt consisting of 48% $Ca(NO_3)_2$, 7% $NaNO_3$, and 45% KNO_3. New salt mixtures are being investigated and developed to overcome current problems with high freezing points.
7. Solid sensible heat storage have been investigated and tested recently, including concrete and castable ceramics as the most promising candidates. The low cost of the solid material has to be balanced with the increased cost of the heat storage design, especially the required heat exchanger.
8. Latent heat storage is a promising technology, as it brings higher storage density and nearly constant temperature. Several materials have been analysed and identified, but so far no commercial high temperature PCM technology is available. The chemical storage technology is also promising, but is even less developed than the latent heat one for concentrated solar power heat storage. Some studies have claimed that ammonia and the SnO_x/Sn reactions may be the most suitable ones, but much more investigation is still needed.
9. Several investigations have been published on the corrosion effect of molten salts in steel and stainless steel tanks. They conclude that the impurities typically contained in commercial grades of alkali nitrates have relatively small effects in corrosion of stainless and carbon steels in molten salts prepared from these constituents.
10. A comprehensive literature review on high temperature thermal storage models has been included. The number of papers addressing this issue is relatively scarce. In general, most of the models available in the open literature deal with solid sensible heat storage. There are also several studies focused on latent heat storage with cylinder-tube geometry. A few other studies were found, including liquid sensible heat storage, latent heat storage in packed beds, and chemical heat storage.

Acknowledgments

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